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Feasibility of Using Fiber Optics for Monitoring Groundwater Contaminants

Lawrence Livermore National Lab., CA

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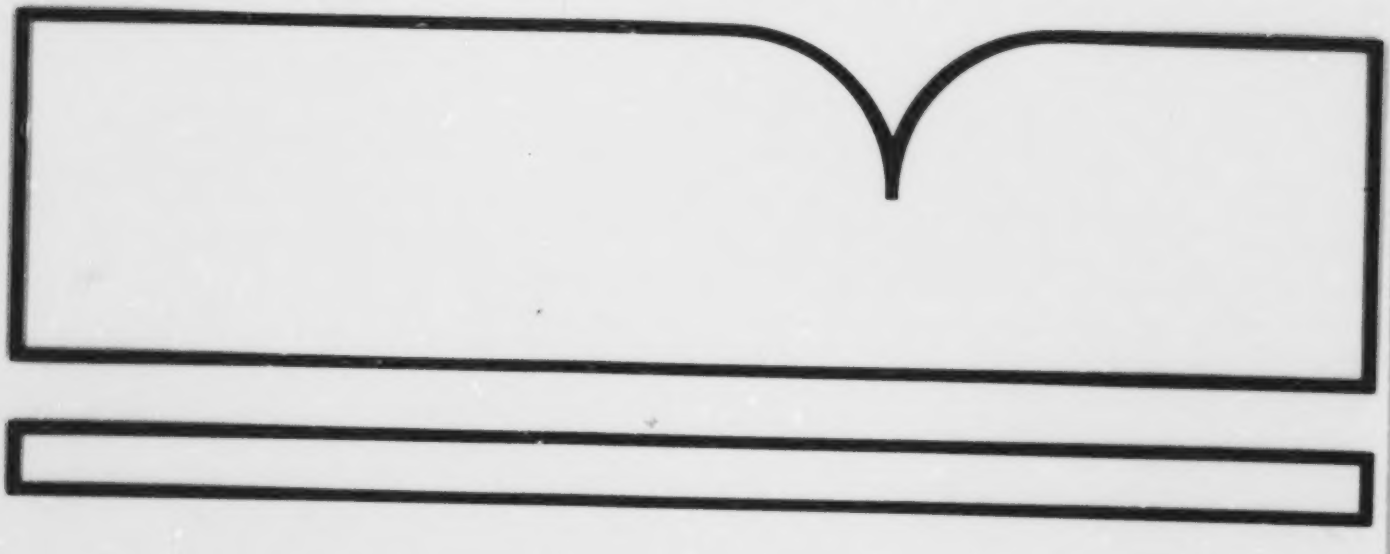

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THE FEASIBILITY OF USING FIBER OPTICS FOR MONITORING GROUNDWATER CONTAMINANTS

by

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CONTENTS

Abstract iii
Figures v
Tables vii
Abbreviations viii

1. Introduction 1
2. Conclusions 2
   Contaminant Detection and Quantification 2
   Tracers 3
   Physical Measurements 3
   Advantages of Fiber Spectroscopy 3
   Limitations of Fiber Spectroscopy 4
3. Recommendations 6
4. Remote Fiber Optic Spectroscopy 7
   Fluorimetry 7
   Remote Fiber Fluorimetry 8
5. Optrodes 25
   Optical Considerations 25
   Chemically Active Systems 35
6. Summary of Experimental Results 42
   Fiber Properties 42
   Sample Characteristics 43
   Chemical Analyses 43
   Tracer Detection 53
   Physical Measurements 53
7. Preliminary Economic Evaluation 70

References 73
Appendices
   A. Signal Levels in Distal Fiber-Optics Fluorimetry 74
   B. Misalignment Tolerance in Remote Fiber Fluorimetry 78
   C. Convection-Driven Capillary Optrode Sampling 81

FIGURES

Number		Page
1	Block diagram laboratory fluorimeter	10
2	Block diagram remote fiber laboratory fluorimeter	11
3	Schematic of optical fiber	13
4	Typical optical fiber	14
5	Optical layout geometric coupler	16
6	Mechanical layout geometric coupler	17
7	Schematic of remote fiber measurement system	18
8	Block diagram of multichannel remote fiber fluorimeter	19
9	Schematic of two-channel remote fiber measurement system	20
10	Schematic of filter fluorimeter	23
11	Filter fluorimeter	24
12	Field-of-view single fiber system	27
13	Field-of-view two-fiber arrangement	28
14	Field-of-view lens optrode	29
15	Schematic of ball optrode	30
16	Field-of-view ball optrode	31
17	Ball optrode	32
18	Schematic of capillary optrode	33
19	Capillary optrode	34
20	Schematic of coated optrode	36
21	Coated membrane optrode	37

FIGURES (Continued)

Number		Page
22	Reservoir optrode	38
23	Schematic of reservoir optrode	39
24	Schematic of self-cleaning optrode	41
25	Power-handling capability of 60 m optical fiber	44
26	Signal vs. sample depth	45
27	Calibration of a Cl^- optrode	46
28	Calibration of fluorescein optrode	48
29	Detection of UO_2^{+2} using optrodes	51
30	Detection of 1 ppm UO_2^{+2} at 100 m	52
31	Organophosphorous optrode	54
32	Detection of 10 ppb rhodamine 6G at 100 m	55
33	Schematic of temperature optrode	57
34	Temperature optrode tip	58
35	Temperature optrode	59
36	Temperature dependence of ruby spectral response	60
37	Calibration of ruby temperature optrode	61
38	Calibration of Nd and Cr glass optrodes	62
39	Schematic of pressure optrode	63
40	Pressure optrode	64
41	Calibration of pressure optrode	66
42	pH dependence of acridine orange fluorescence	67
43	pH dependence of fluorescein fluorescence	68
44	Calibration of neutral acriflavine pH optrode	69
A-1	Illumination in simple termination for remote fiber fluorimeter	75

TABLES

Number		Page
1	Transmission Efficiency vs. Distance (40 db/km Loss)	42
2	Signal Intensities for 1 ppm of Tracer Compounds at 100 m Using RFF	56
3	Operational Scenario for Groundwater Analysis	70
4	Individual Component Cost of Groundwater Analysis	71
5	Cost Comparison Between Analyses Using Collected Samples and In situ Measurements Using Fiber Optics (1 year and 5 years)	72
B-1	Misalignment Loss in Remote Fiber Fluorimetry	79

ABBREVIATIONS

cm^3	- cubic centimeter
cps	- counts per second
CW	- continuous wave
db	- decibel
Eh	- oxidation potential in volts
IR	- infrared radiation
l	- liter
lb/in^2	- pounds per square inch
M	- molar
m	- meter
ml	- milliliter
mo	- month
nm	- nanometer (10-^9m)
pH	- potential of hydrogen (acidity)
ppb	- parts per billion
ppm	- parts per million
redox	- reduction-oxidation
s	- second
V	- volt

SECTION 1

INTRODUCTION

The need to provide the nation with assured safe sources of drinking water is unquestionable. Groundwater has traditionally been considered to be of the best quality, because it has very low microbial concentrations and is relatively free of sediment and other contaminants associated with surface water. Approximately one-half of the drinking water used in the United States is derived from underground aquifers.

Regulations promulgated under the Safe Drinking Water Act of 1974 set forth the National Interim Primary Drinking Water Standards which are maximum permissible levels of certain inorganic and organic pollutants. Further authority to protect groundwater is provided by the Clean Water Act of 1977. Regulations under this act extend water quality protection to all ambient waters, the ultimate sources of drinking water.

Unfortunately, groundwater is not immune to contamination. It is connected to the surface at recharge areas and can be breached by wells or other excavations which allow contaminants to enter from above. An especially important source of groundwater contamination is the hazardous waste disposal site. There are an estimated 30,000 to 50,000 hazardous waste sites in the United States, and the most serious potential environmental impact from these facilities is groundwater contamination.

This report focuses on the feasibility of making remote in situ groundwater contamination measurements over optical fibers using laser-induced fluorescence spectroscopy. The ability of this technique to monitor key contaminants in the sub parts-per million range is assessed as are its potential economic advantages.

SECTION 2

CONCLUSIONS

The feasibility of making remote measurements (up to 500 m), where fiber optics are used to connect analytical measurement points and the analyzer, has been established. This approach has the potential of qualifying and quantifying groundwater contaminants in the sub-parts-per-million (ppm) range. Tracer materials can be detected below one part-per-billion (ppb). In addition, measurements can be made of some of the physical properties of groundwater which affect contamination. Finally a preliminary economic study indicates that this method may be less expensive than extant monitoring techniques.

CONTAMINANT DETECTION AND QUANTIFICATION

This portion of the effort focused on the measurement of inorganic and organic chloride. In addition, preliminary measurements were made on aldehydes, alcohols, sulfate and pesticides. The results to date are as follows:

(a) Inorganic chloride - Analysis is accomplished using the reaction of Cl^- with silver fluoresceinate to release the fluorescent fluorescein. Data exists to 10 ppm with projections of sub-ppm sensitivities.

(b) Organic chloride - A general analytical method based on the complete oxidation of organic chloride by chromic oxide to yield Cl^- and the subsequent reaction with silver fluoresceinate is being developed. At present only the two individual reactions have been successfully tested. Detection limits appear to be dependent on the AgCl solubility.

(c) Aldehydes - Measurement is accomplished by the quenching of normally fluorescent Schiff reagents by aldehydes.

(d) Alcohols - Selective oxidation of alcohols to aldehydes is accomplished and then the degree of quenching of Schiff reagents is determined.

(e) Sulfate - The release of fluorescent chloranilic acid from barium chloranilate by the reaction with $SO_4^=$ is the chosen analytical method.

(f) Pesticides - An initial effort indicated that an enzymatic reaction

based on cholinesterase inhibition by pesticides is a good detection method. The complexity of the approach makes it a subject for re-evaluation.

TRACERS

The use of tracers in groundwater is important both for research purposes and for following the route of contamination from specific injection sources. In recent work, fluorescent tracers, such as Rhodamine 6G, brillant sulpho-flavine and fluorescein were evaluated at concentrations of 1 part-per-million and a range of 100 meters. Extrapolation of the existing data indicates that at 300 meters detection limits could reach 1 part-per-billion or less.

PHYSICAL MEASUREMENTS

Measurements of temperature, pressure, pH and Eh (oxidation potential) have also been accomplished. These measurements are important because they give information about the contaminant species which is present. Temperature can be measured over a wide range to 0.1°C and over a restricted span to 0.01°C from 20 to 250°C. Pressure can be resolved to 0.01 lb/in^2. pH is resolvable to 0.5 pH units over the complete pH scale. Eh can be determined to 0.1 V from 1.1 to -0.6 V. Methods for measuring pH and Eh are presently being developed further.

ADVANTAGES OF FIBER SPECTROSCOPY

The first year's work has led to the conclusion that there are many key advantages to the use of fiber optics in monitoring contaminants. These include:

(a) Geometric flexibility - Fiber optics makes it possible to perform analyses, using optical spectroscopy and small sensor probes, where there is no "line-of-sight" and where the samples are hard to reach.

(b) Environmental versatility - Measurements can be made, over fiber optics, where the sample is hot, cold, radioactive or dangerous.

(c) Real-time analysis - Analytical information is available in a matter of minutes because of the fast response time (approximately 1 minute) of the fiber optic system and because there is no sample collection.

(d) Multiple analyses - Up to 50 locations can be monitored using fiber optic probes (1 for each contaminant at each location) using a single fluorimeter housed at a central location.

(e) Sample integrity - Elimination of sample collection and its multiplicity of drawbacks, coupled to the fact that fiber optic probes cause no sample alteration, assures sample soundness.

(f) Instrument reliability - Placement of the optical spectrometer in a benign environment at a central accessible location makes routine maintenance and checkout possible and assures that calibration will be preserved.

(g) Physical size - Optical fibers are small, lightweight, and low volume which makes them easy to handle and small enough to place in punched holes (rather than drilled wells). They are also rugged and immune to electromagnetic inference.

(h) Cost effectiveness - Fibers are inexpensive and the expense of a single fluorimeter is nominal when distributed over many sample stations. Economic savings are further assured as no sampling labor is required and because the man-hours to operate a 50-sample processor are minimal.

LIMITATIONS OF FIBER SPECTROSCOPY

Several limitations have been observed during the course of this program. They are primarily related to the current state-of-the-art in fiber optic technology. They have been overcome sufficiently to accomplish the goals of this effort. As fiber technology improves, performance can be upgraded. Particular areas that need attention include:

(a) Spectral coverage - Optical transmission through the fibers is essentially restricted to the visible region. The violet and ultraviolet can be used under limited conditions as can parts of the near-infrared, but the mid- and far-infrared are not accessible. (Appendix A discusses propagation of light through the fibers.)

(b) Useable technologies - Only fluorimetry, absorption, refractometry, scattering and reflection measurements can be made in the visible range.

(c) Range restrictions - Analyses are confined to 500 meters in the visible and a few tens of meters in the ultraviolet due to power losses over the length of the optical cable. This loss is further complicated by spectral attenuation and change in numerical aperture as a function of fiber length (because the laser beam under-fills the fiber).

(d) Power limits - The inability of extant fibers to handle high irradiation levels is a major drawback in remote fiber fluorimetry (RFF). Thus the trade-offs between input power and sensitivity (RFF response is linear with irradiation level), and input power and distance had to be carefully done.

(e) Spectral background - The fibers presently being used are designed for communications applications and have impurities of a spectral

nature which can give fluorescence and Raman background. This can be overcome by selecting fibers with low fluorescence characteristics and by using special Raman data handling methods for background discrimination.

(f) Hardware deficiencies - The need for improved commercial accessories has become evident. Better connectors, terminations, switches, etc., which maintain the optical integrity necessary for laser spectroscopy, have had to be specially built for this program. (Appendix B discusses losses due to the misalignment of two fibers.)

SECTION 3

RECOMMENDATIONS

The investigation through FY-82 has indicated the value of the remote fiber spectroscopy approach. The conclusions which can be drawn at this juncture also indicate that more precise goals have to be established if the objectives of this work are to be met. Four recommendations are appropriate at present.

(a) This investigation has demonstrated the versatility of the remote fiber spectroscopy system for the analysis of several water contaminants, but no single species has been looked at in sufficient detail to assure that sensitivity and specificity requirements can be met. It is, therefore, recommended that further investigation be focused on the detailed measurement of individual species.

(b) At the beginning of this investigation no specific species were pointed out as the key contaminants of interest. It is, therefore, recommended that the initial priorities be established as follows: inorganic chloride, organic chloride, sulfate, aldehydes and pesticides.

(c) At the present time it is not clear how the remote fiber spectroscopy systems are to be evaluated and tested. It is, therefore, recommended that under this program a brass board system be made for each species of interest and then tested in the laboratory, under simulated field conditions, and in the field.

(d) A method has not been established for taking the results of this investigation and using them under field conditions. It is, therefore, recommended that technology transfer to potential engineering and manufacturing companies be accomplished in a timely manner.

SECTION 4

REMOTE FIBER OPTIC SPECTROSCOPY

The in situ analysis of water samples for trace contaminants has been considered a technically challenging problem. Until the advent of the fiber optic approach it was decided to perform laboratory analyses on samples collected in the field in spite of the many difficulties. Such procedures are time consuming and inefficient from a labor viewpoint. Sample integrity may also be compromised by foreign material being taken in by the collector or by contact with the container. Furthermore, collecting samples is either not possible at all in some locations or prohibitively expensive because of the need to drill wells. Delays between collection and analysis and the lack of real-time data may make it difficult to follow the development of a rapidly changing situation. Finally, there is the danger that samples may become lost or mislabeled.

By doing in situ monitoring, many of these objections are overcome. Several new considerations, however, must be addressed. These include sensitivity, specificity, the depth of the sample and its accessibility from the surface, drilling economics, and the data processing required to provide useful information.

After an evaluation of the contaminants in drinking and groundwaters of most concern to the U.S. Environmental Protection Agency (EPA), it was determined that optical spectroscopy, and in particular laser-induced fluorescence spectroscopy, met the prerequisite requirements for in situ monitoring. Optical methods, however, require a "line-of-sight" geometry which in the past precluded this approach for underground measurements. This has now been overcome by the use of thin flexible optical fibers (light pipes) which provide an optical connection between the analyte and the analyzer. Thus, all the advantages of optical spectroscopy can now be achieved underground, at locations at least up to 500 meters from the on-ground laser source and spectrographic analyzer.

FLUORIMETRY

To fully define fluorescence would require a discussion whose length would be grossly disproportionate to the contents of this report. For the sake of completeness, therefore, only the basic rudiments, as they apply to the present investigation, are presented.

When a quantum of light impinges on a molecule there is a probability,

dependent on the wavelength, that the light will be absorbed. The process is nearly instantaneous and results in the visible and UV absorption spectra that is characteristic of many molecules. Once in the excited state, the molecule typically loses a small fraction of the excitation energy and then returns to the ground state by the emission of radiation. Consequently, the emitted light will generally be of a longer wavelength than the absorbed. Depending on the nature of the excited state, the process can be short lived (fluorescence) or long lived (phosphorescence--times usually greater than 10^{-4}).

Fluorescence is usually induced by use of ultraviolet and visible radiation. Monochromatic laser sources are normally used to excite the molecule because they provide a convenient source of high intensity radiation and because their monochromaticity assures that all of the available energy is fully utilized. This gives maximum sensitivity. It should be noted, however, that the exciting radiation must be at a wavelength that the substance to be detected will absorb and reradiate.

Fluorescence is exhibited both by free atoms and by molecules. It can occur in the gaseous, liquid, and solid states, although not necessarily in all three phases of the same substance. The fluorescence effect at the atomic level is well understood. Fluorescence in molecules is a more complex phenomenon since the electronic excitation and de-excitation processes may be accompanied by secondary changes in the vibrational and rotational energy of the molecule. It is molecular/ionic fluorescence that is of interest in pollution monitoring. Fortunately, the ultraviolet-visible systems are well defined for the species of interest to EPA.

Materials that fluoresce (or phosphoresce) naturally, those that can be converted to fluorescent compounds (fluorophors), and those that extinguish fluorescence can be determined quantitatively by fluorimetry. Compounds in a mixture can generally be distinguished from one another because:

(a) compounds that absorb radiation at the same frequency typically emit radiation at different frequencies,

(b) compounds that emit at the same frequency often absorb at different frequencies, and

(c) transitions of different lifetimes can be readily distinguished by modern light-measuring techniques.

Indeed, the advent of modern laser techniques has made fluorimetry the most sensitive spectrophotometric analytical technique. (1-3)

REMOTE FIBER FLUORIMETRY

Laser-based remote fiber fluorimetry (RFF) is a new analytical technique that offers the potential to measure and monitor on-line, and in near-real-time, trace (ppm) to substantial (g/l) concentrations of selected chemical species in a variety of environments from one central monitor that is remote

to all measurement points.

The remote in situ detection and quantification of a variety of species in aqueous systems is made possible by the use of fiber optics coupled to a laser fluorimeter. A laser is focused onto an optical fiber, the laser light travels through the fiber, excites fluorescence in the sample, and the returning wide-angle beam is focused onto the slits of a double monochromator. The fluorescence spectra are processed and presented using a minicomputer and graphic display. Where preselected species are to be measured, the monochromator is replaced by narrow-band optical filters and the minicomputer is supplanted by hard-wired electronics. This results in increased sensitivity and reliability at reduced cost but with the loss of versatility.

Laboratory Fluorimeter

Sensitive, high resolution, versatile laboratory fluorimeters, such as used in this program, are based on a Raman spectrometer design such as shown in Figure 1. The major components of this system are:

(a) An argon ion laser,

(b) Laser optics to couple the laser beam to the sample,

(c) A sample holder,

(d) Collection optics to gather the emitted fluorescence and focus it on the slit of the monochromator,

(e) A double monochromator with holographic gratings for spectral sorting and stray light rejection,

(f) A photomultiplier tube (PMT) to receive the fluorescence signal,

(g) Photomultiplier optics to couple the monochromator and PMT,

(h) Detection electronics to collect the output of the PMT,

(i) A minicomputer to process the received data, and

(j) A chart recorder to display the fluorescence spectrum.

Furthermore, to assure that the maximum sensitivity and information output are obtained, a variety of CW, pulsed, and dye lasers are available for irradiation. Pulse-counting electronics can be used when necessary.

Laboratory Remote Fiber Fluorimeter

The laboratory fluorimeter is adapted for remote fiber operation by replacing the laser optics with a lense to focus the laser power onto the fiber and by substituting a coupler for the sample holder (Figure 2). The spectrometer portion of the system remains intact.

LABORATORY RAMAN/FLUORESCENCE SPECTROMETER

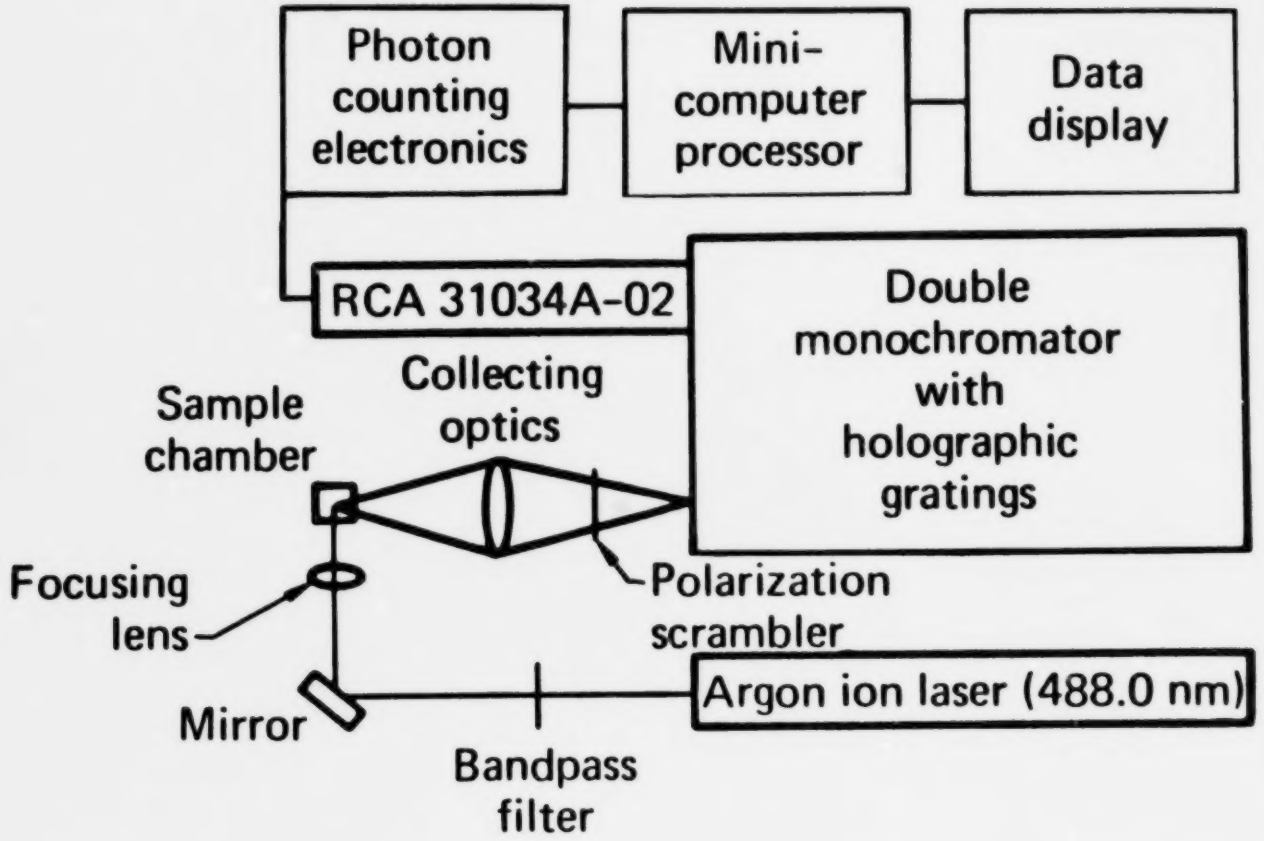


Figure 1. Block diagram laboratory fluorimeter.

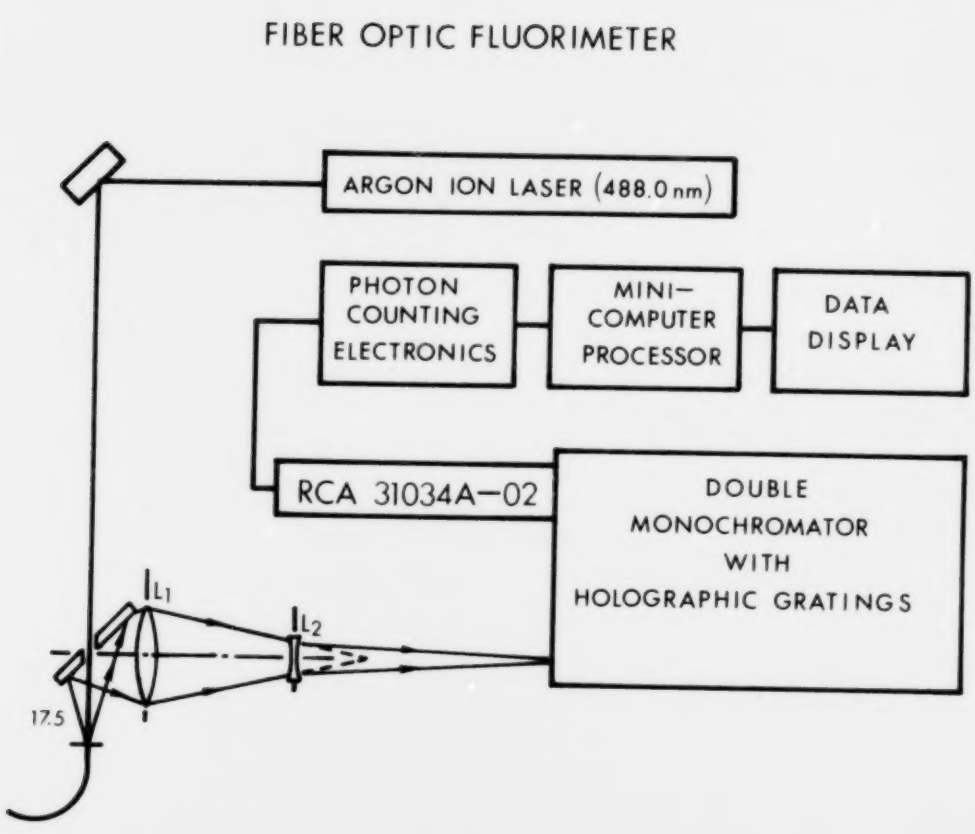


Figure 2. Block diagram remote fiber laboratory fluorimeter.

Fiber Optics--

The concepts of fiber optics became commercially feasible in the 1950's and their early use was described in two articles in Nature.[4,5] The field of fiber optics has since grown to include medical, military, and industrial applications with significant recent interest by the communications industry.[6]

The communications industry, faced with a need for larger bandwidth communications cables than were possible with electrical wires and radio, developed long-distance fiber-optic strands capable of transmitting over distances of several kilometers with remarkably little attenuation. A whole technology of special connectors and input-output terminations have been invented to use fibers conveniently. Advances have successively expanded the wavelength range of such fibers until they now cover most of the visible and near-infrared.

The optical fiber is a smooth strand of transparent material designed to conduct light with high efficiency (Figures 3 and 4). The light entering an optical fiber is reflected from the walls by total internal reflection. This reflection is nearly devoid of loss because of the transparent layer (cladding) of material of lower refractive index that coats the fiber walls. This cladding also serves to protect the interface from dust and scratches and isolate fibers from one another when they are used in bundles.

Optical fibers are made of glass, plastics, fused silica, or combinations of these materials. Depending on application, the fibers are available with numerical apertures as low as 0.17 (low-loss transmission) and as high as 1.04 (image tube faceplates). The attenuation of these fibers is as low as 1 db/m in the near IR. For more detail on the propagation of light in these fibers see Appendix A.

Light Source--

Laser light of an appropriate wavelength is normally used to stimulate the fluorescent radiation. Such highly monochromatic beams of moderate power are needed to give the brightness required for illuminating the fiber properly and can readily be focused down to spots of a few micrometers. For research purposes, the laser-based RFF work presently employs four different types of lasers. These include:

(a) A high-power krypton laser capable of multiple wavelength operation, including red and UV wavelengths, supplemented by a tunable dye-laser accessory;

(b) Two high-power argon lasers, also with multiple wavelength capabilities including the UV and equipped with mode locking, frequency doubling, synchronous pump, and etalon capabilities;

(c) A helium-cadmium laser having both UV and blue outputs at medium power levels; and

(d) A high repetition rate, high-power, pulsed nitrogen laser with provision for pumping a dye laser.

SCHEMATIC OF A TYPICAL CLAD FIBER

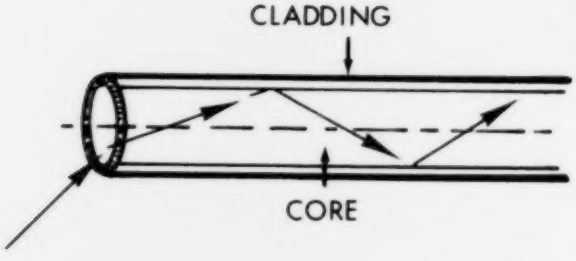


Figure 3. Schematic of optical fiber.

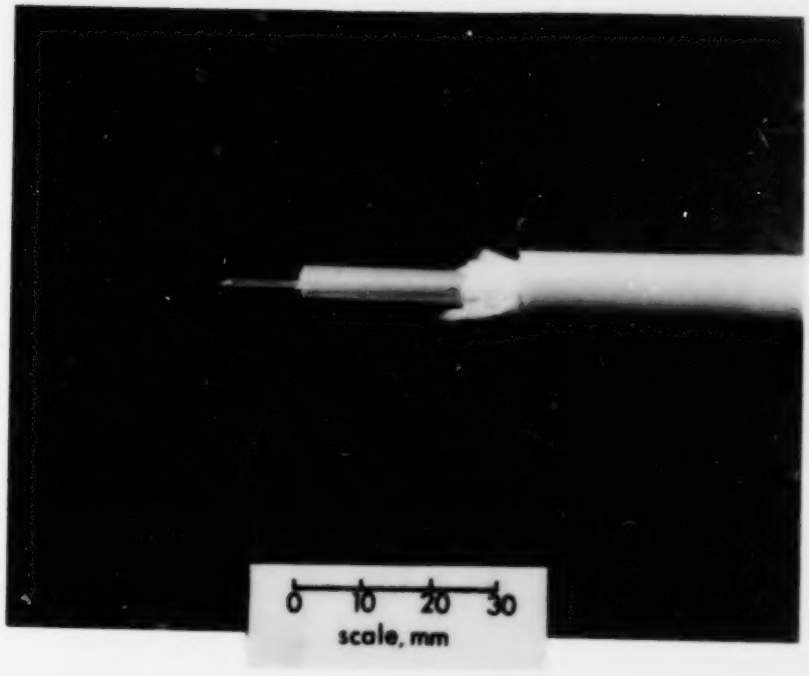


Figure 4. Typical optical fiber.

Coupler--

First, the laser light must be focused onto the end of the fiber. Secondly, the stimulated fluorescence or echo light must be returned along the same fiber and directed to a spectrometer or filter photometer to quantitatively measure its intensity. These objectives require separating the outgoing and returning light by their direction. A dichloric mirror can also accomplish this separation by wavelength discrimination. This is very efficient, but rather inflexible. Finally, the larger divergence or aperture of the returning light can be used to effect separation by using concentric input and output beams. Here a laser is focused onto an optical fiber through a specially designed mirror with a hole in it (Figures 5 and 6). The laser light travels through the fiber, excites fluorescence in the sample, and the returning wide angle beam impinges on the mirror, rather than passing through the hole, and is focused onto the slits of the monochromator.

Spectrometer and Data Handling--

The collected light is refocused at f/8 into a Spex No. 14018 0.75-m focal length double monochromator equipped with holographic gratings blazed at 500 nm. The monochromatized light is reimaged at f/2 onto a cooled (-20°C) RCA C31034A GaAs photomultiplier (PMT) in a Products for Research RF-TSA cooled housing. The PMT is operated at <2000 V using a Power Design 2K-15 adjustable filtered high voltage source. The photoelectron pulses are conditioned, windowed, and counted by a photo counting system consisting of Ortec Model 9301 and 9302 amplifiers and an Ortec Model 9349 rate meter. The output of the rate meter is fed to a Hewlett-Packard Model 3456A electrometer having a HPIB interface and controlled by a Tektronix Model 184 time mark generator. The electrometer is in turn coupled to a Tektronix Model 4051 graphics processor having a flexible disk attachment, a LSI-11/23 computer (for data processing and management), a Tektronix Model 4631 hardcopy generator, and a Tektronix Model 4662 plotter.

All research and development data were obtained using this and another similar system.

Conceptual Fieldable Remote Fiber Fluorimeter

A schematic of how a fieldable remote fiber measurement system could operate is shown in Figure 7. It is anticipated that all equipment, except the fibers, will be housed in a trailer or other mobile device. The system is similar to the laboratory spectrometer in design except for the laser and spectral sorter. The system will, in all probability, have multichannel (multispecies) capability (Figure 8). Here several fibers looking for the same contaminant at several locations can feed into a single channel. For example, measurement of 4 contaminants at each of 10 sources required 4 channels and 40 fibers (10 per channel). Figure 9 shows the layout for a 2-channel system. This design provides for the measurement of 1 each of 2 contaminants at 100 percent duty cycle. Measurement of 4 sampling points for 2 species reduces the duty cycle at any source to 25 percent. If a large number of species are to be measured at a high repetition rate a polychromator should be used. Filter wheels can be used when there are many analyses that are to be repeated at long

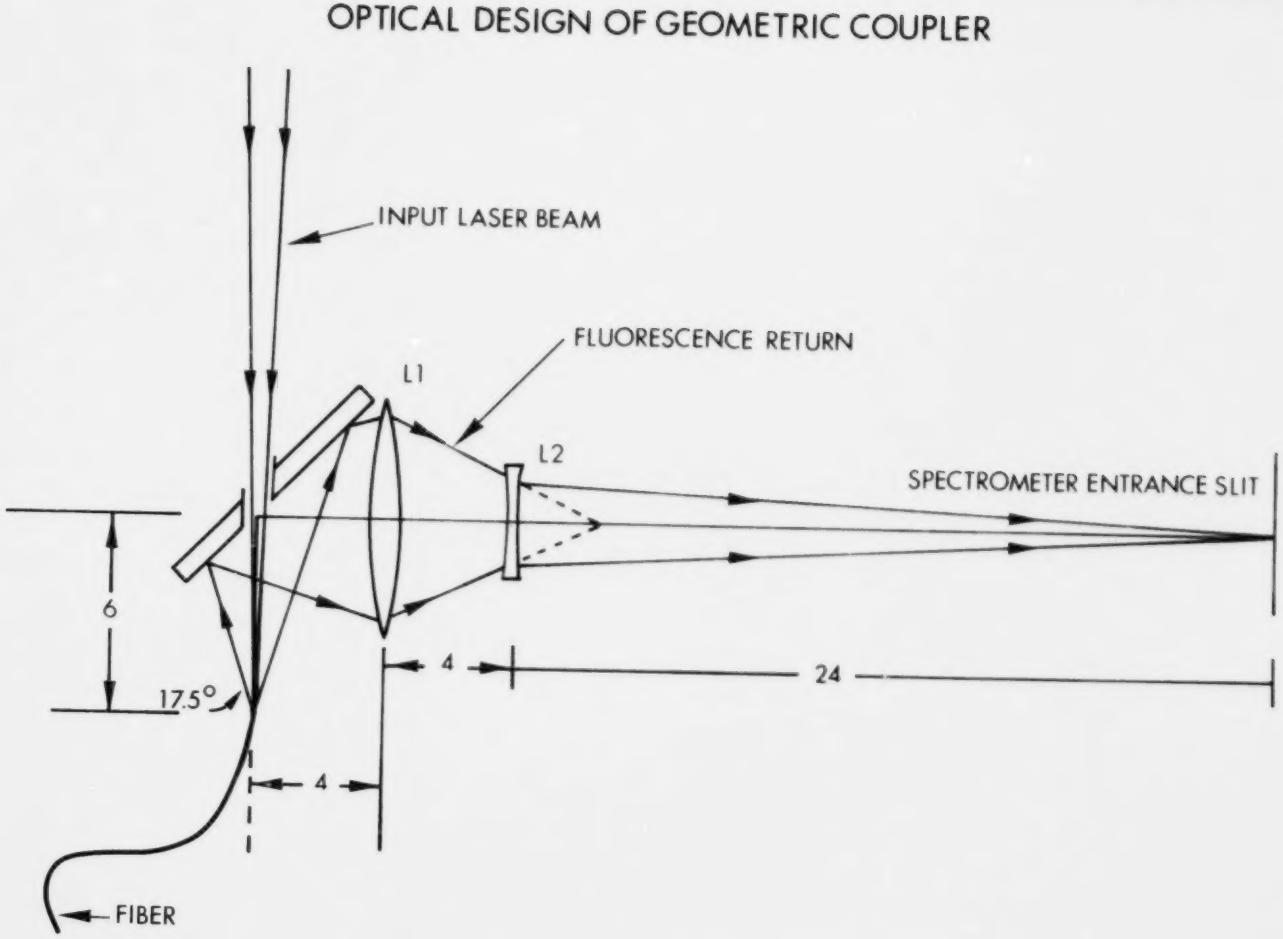


Figure 5. Optical layout geometric coupler.

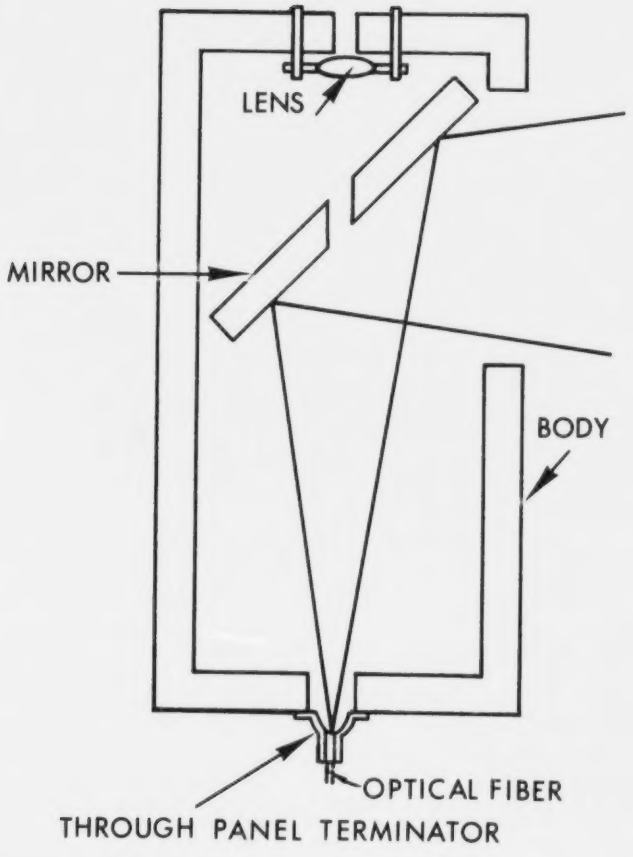


Figure 6. Mechanical layout geometric coupler.

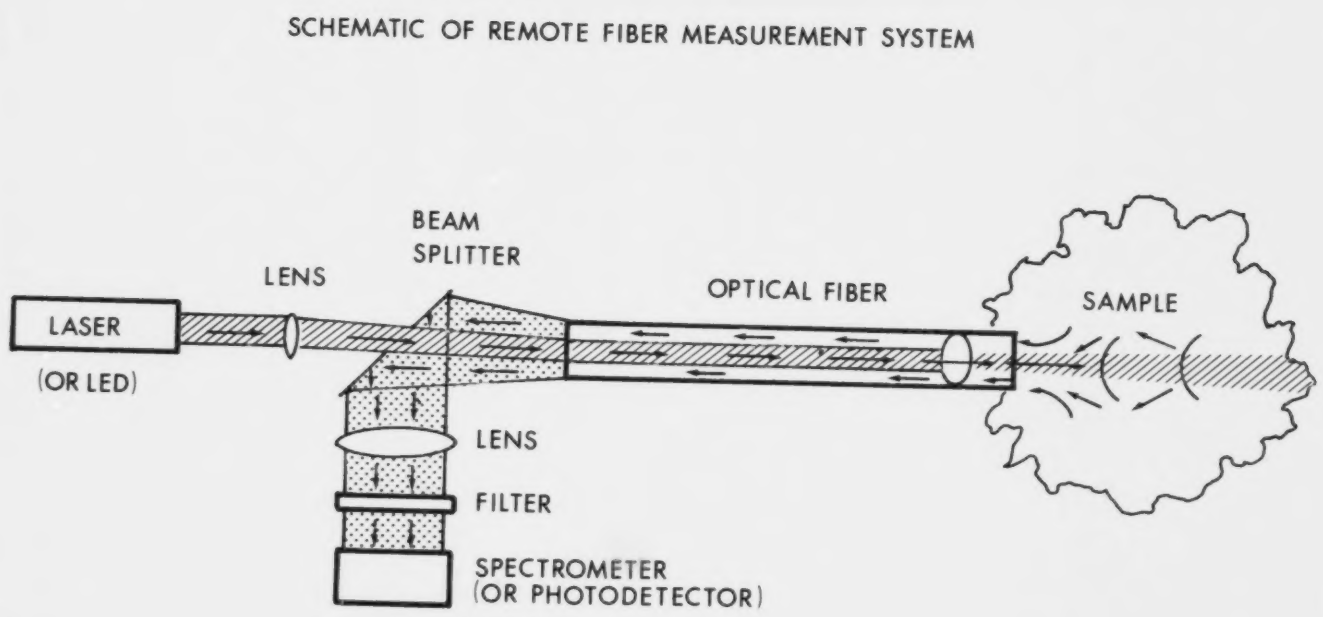


Figure 7. Schematic of remote fiber measurement system.

BLOCK DIAGRAM OF REMOTE FIBER
FLUORIMETER MULTIPOINT SAMPLING NETWORK

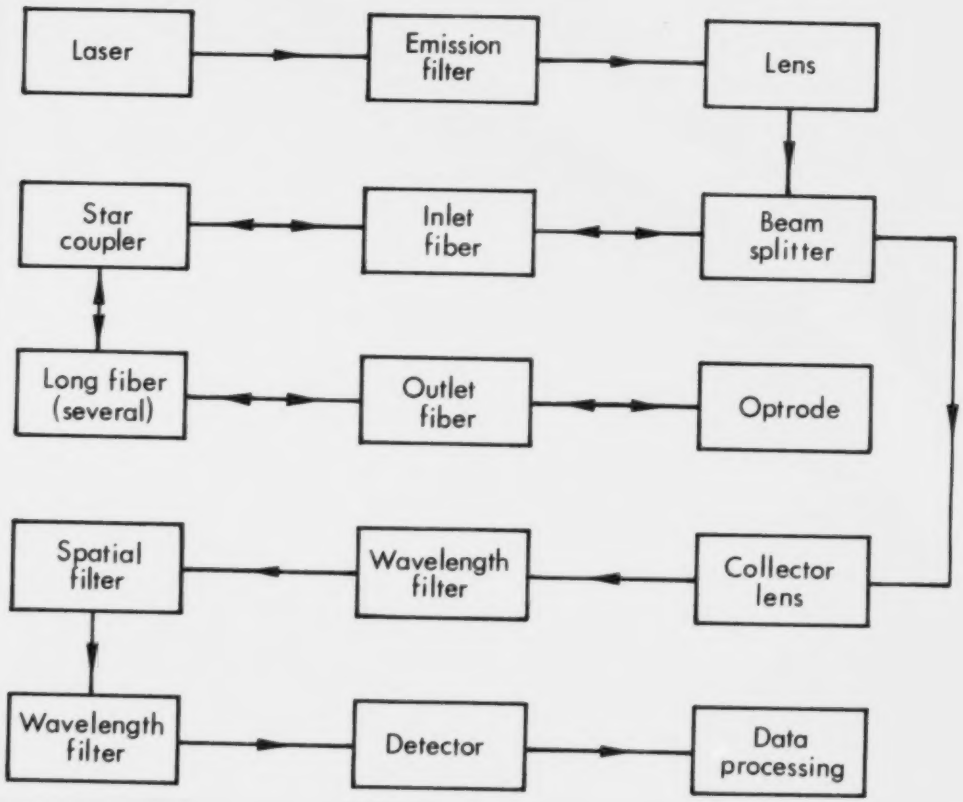


Figure 8. Block diagram of multichannel remote fiber fluorimeter.

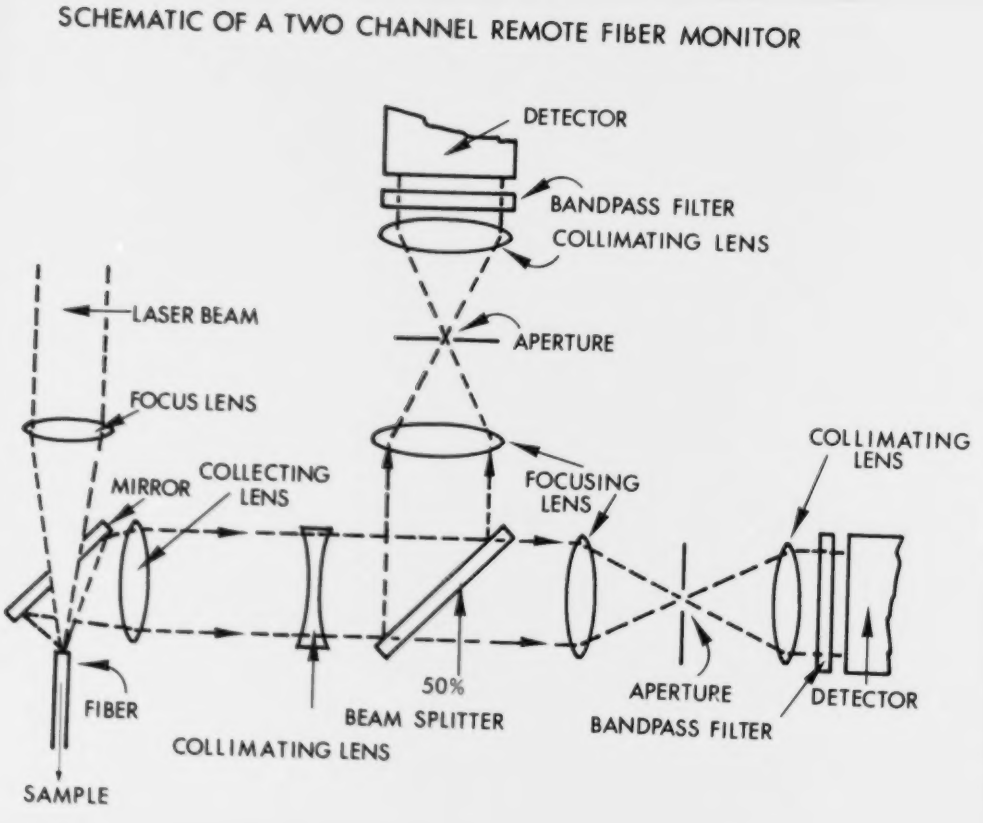


Figure 9. Schematic of two-channel remote fiber measurement system.

intervals (several hours).

Trailer--

The fieldable system should be housed in a mobile laboratory with the following:

(a) Heating,

(b) Air conditioning,

(c) Humidity control, and

(d) Electrical generator.

The trailer will house:

(a) Fiber optic switching circuits,

(b) Air-cooled argon-ion laser,

(c) Fluorimeter,

(d) Photomultiplier with cooled housing,

(e) Electronics,

(f) Microprocessor (data handling and processing),

(g) Display, and

(h) Calibration equipment.

Concept Fieldable Laser--

The fieldable laser, as presently conceived, will have the following properties:

(a) It will be a CW argon ion laser to provide optimum irradiation frequencies,

(b) It will be air-cooled to circumvent the logistics of water-cooled systems,

(c) It will contain an etalon to assure spectral purity,

(d) It will have a minimum output of 30 mW at 488.0 and 514.5 nm to guarantee system sensitivity, and

(e) It will be lightweight and rugged to assure mobility.

Concept Fieldable Laser Fluorimeter--

The fieldable laser fluorimeter is much more than a "hardened" version of a laboratory system.

(a) It should be very simple,

(b) It should be as sensitive as possible,

(c) It should be dedicated to those specific species of interest, and

(d) It should be simple to operate, rugged, and meet realistic power and weight requirements.

Inasmuch as the spectrometer will be used in a field laboratory, the spectral sorter, which is the key component, can be constructed as shown in Figure 10. This instrument uses filters rather than gratings, is small and lightweight, and is sufficiently rugged to maintain optical alignment. A breadboard version of this unit has been constructed and successfully tested (Figure 11). Multiple channel capability is attainable by substituting filter wheels for the single band pass filters.

As stated previously, a polychromator is a possible alternative to the filter system.

FILTER FLUORIMETER

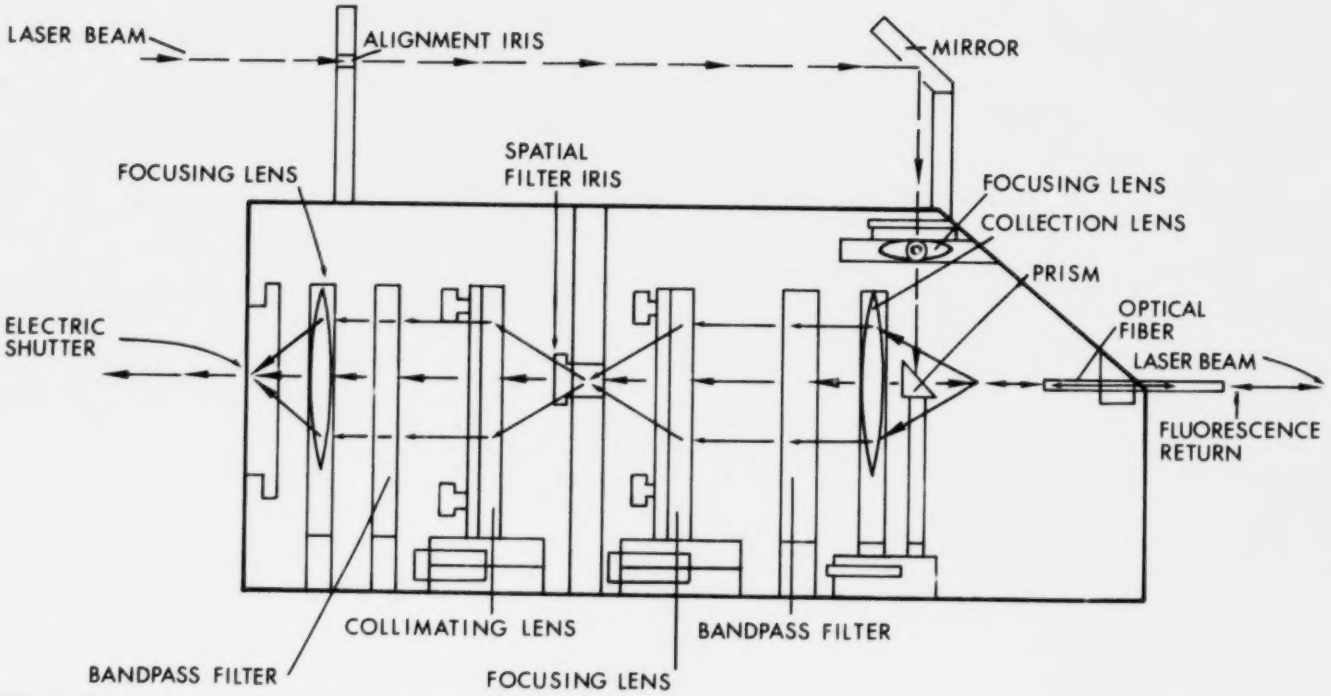


Figure 10. Schematic of filter fluorimeter.

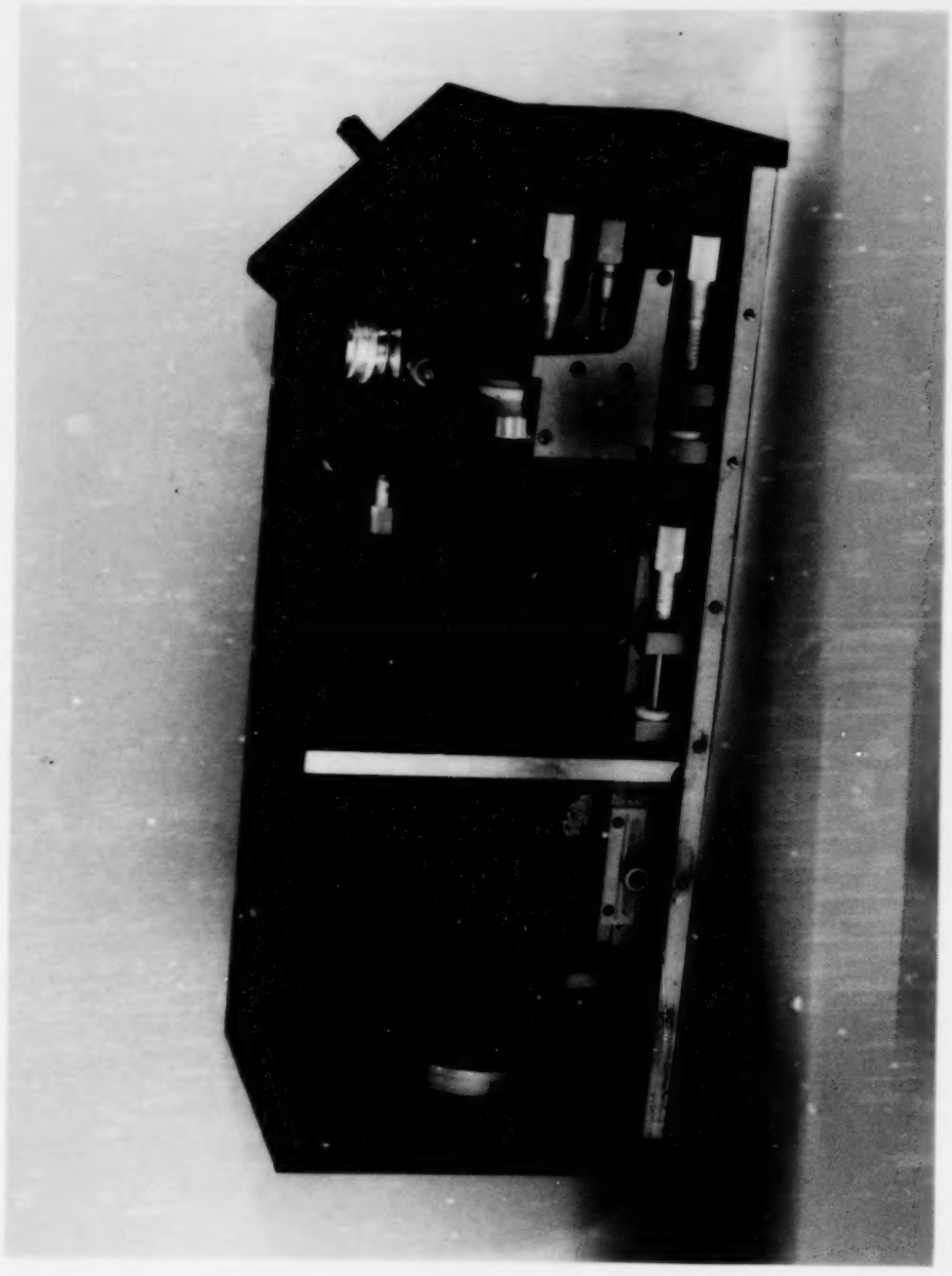


Figure 11. Filter fluorimeter.

SECTION 5

OPTRODES

Optical fibers are fundamentally wave guides for optical frequencies. These properties have been discussed in Section 4. In Section 5, the role of fibers in transporting the irradiating energy from the laser, illuminating the sample, and returning the resultant fluorescent light to the spectrometer is discussed. Emphasis is placed on the use of modified fiber terminations to enhance sensitivity and specificity, and increase the number of species which can be measured. These modified fibers have been given the name optrodes.(7,8)

An optrode, by analogy with electrode, is the sample-contact termination of an optical fiber. This concept is important because an optrode can be used to:

(a) Enhance sensitivity through optical engineering,

(b) Enhance sensitivity through chemical reactions,

(c) Reduce background and interferences by both optical and chemical means,

(d) Detect species which are not naturally fluorescent; i.e., an optrode can be designed to hold a reactive reagent to produce a material whose fluorescence reflects the species to be identified.

(e) Measure physical properties such as temperature, pressure, pH, and oxidation potential.

OPTICAL CONSIDERATIONS

When using fiber optics in chemical analysis the objective is to observe as large a sample volume as possible for maximum sensitivity. It is also necessary to assure that the field-of-view, the transmission, and other optical properties of the fiber remain intact during a measurement or from measurement to measurement. The selection of the illumination and collection configuration, therefore, must take into account that the ultimate application is in the field and optical ruggedness is a consideration.

Selection of a One- or Two-Fiber System

One decision which had to be made early in the program was whether to use

a 1- or 2- fiber design; i.e., transmit laser light and receive the fluorescent signal on the same fiber or on separate ones. The single fiber approach has two primary considerations:

(a) The field-of-view of a single fiber is very small and, therefore, only a minimum volume of sample is illuminated (Figure 12).

(b) It is necessary to separate the input laser light from the returned fluorescent signal.

The dual fiber approach has the following characteristics:

(a) The observed sample volume is larger (Figure 13).

(b) The system is severely limited by the slightest fiber misalignment (Experience with this system indicates it has the potential to be an ultrasensitivie seismograph.)

Based on the misalignment difficulties, it was decided to use the single fiber system for the initial study. (This is consistent with Figures 2, 5, and 6, Section 4). The two-fiber approach will be reevaluated after it is determined if a system can be engineered to maintain alignment under adverse conditions.

Ball Optrode

Once the single fiber approach was selected, in the earliest experiments fluorescence was observed by simply placing the end of an optical fiber in a sample cell. It was soon realized, however, that improved performance could be obtained by increasing the angle of acceptance of the fiber to collect a greater part of the fluorescence emission. This is easily achieved by inserting a lense in front of the fiber (Figure 14). A better way to do this is to place the fiber in a capillary tube which holds a 1/8-inch-diameter sapphire ball (Figure 15). This provides an apparent larger diameter for observation of the sample through the fiber (Figure 16). It is not possible to diagrammatically compare the effectiveness of the ball optrode (Figure 16) with the plain termination (Figure 12). The ball optrode effectively refocuses the fluorescence light back into the fiber. This eliminates problems such as edge, wall, and boundary layer (in flowing samples) effects and sensitivity to sample heterogeneity which are inherent to the plain termination. The components for the ball optrode are very simple and the ball optrode is quite small (Figure 17). The ball optrode is very important because it is the basis for many of the chemical and physical optrodes.

Capillary Optrode

Still further increases in sensitivity can be gained by coupling an internally mirror-coated capillary to the end of the fiber. This creates a waveguide effect for light that increases the observed sample depth and simultaneously collects more of the emitted fluorescence signal. This arrangement is shown schematically in Figure 18. An actual capillary optrode is shown in Figure 19. One of the problems with a capillary optrode is sample exchange time. Diffusion is too slow, and the use of an external pump negates, to a

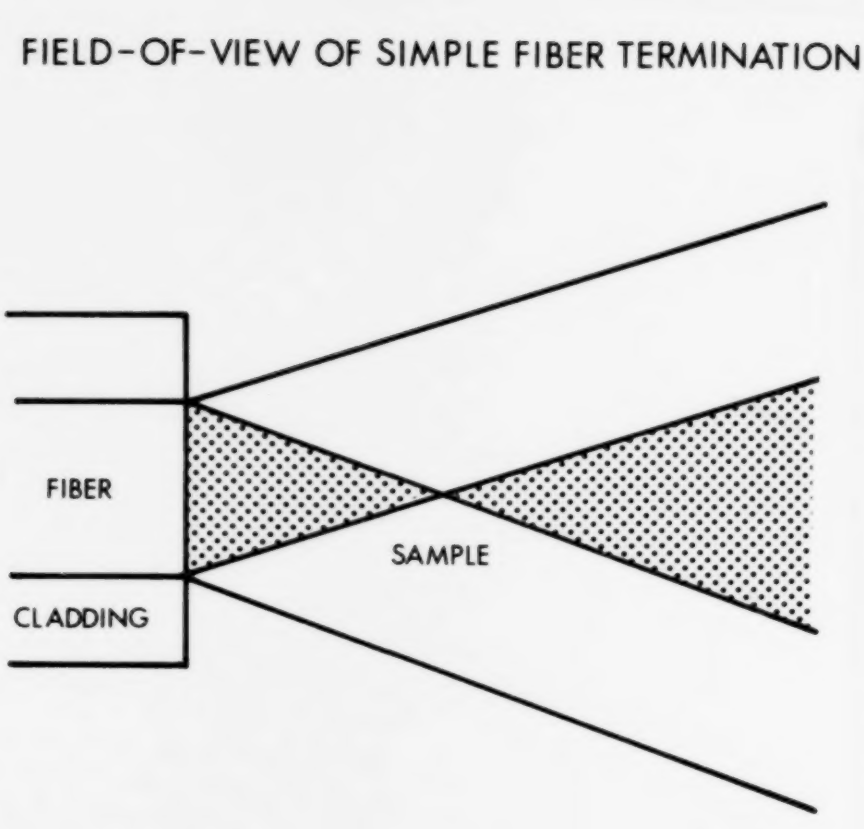


Figure 12. Field-of-view single fiber system.

DOUBLE FIBER TERMINAL FOR REMOTE FIBER FLUORIMETER

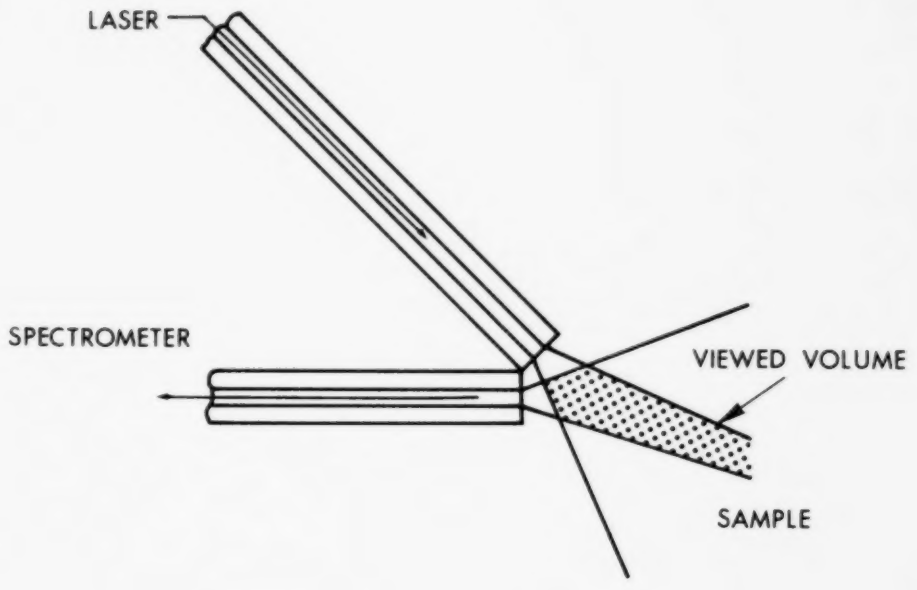


Figure 13. Field-of-view two-fiber arrangement.

BENEFITS OF LENS IN RFF OPTRODE

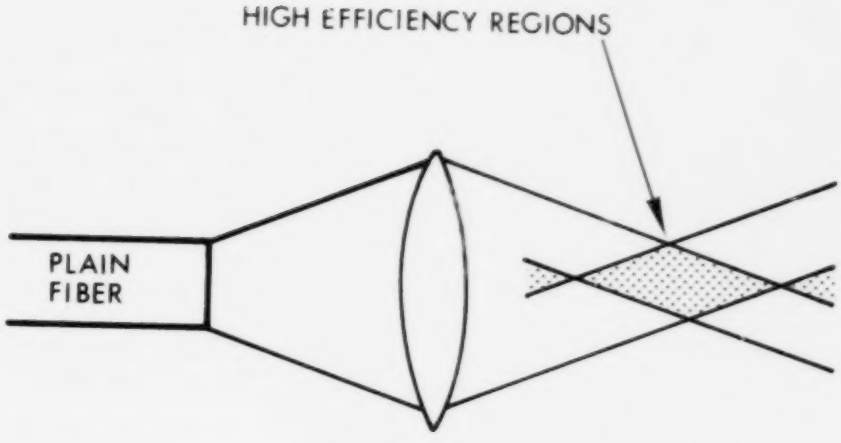


Figure 14. Field-of-view lens optrode.

BALL "OPTRODE" FOR REMOTE FIBER FLUORIMETER

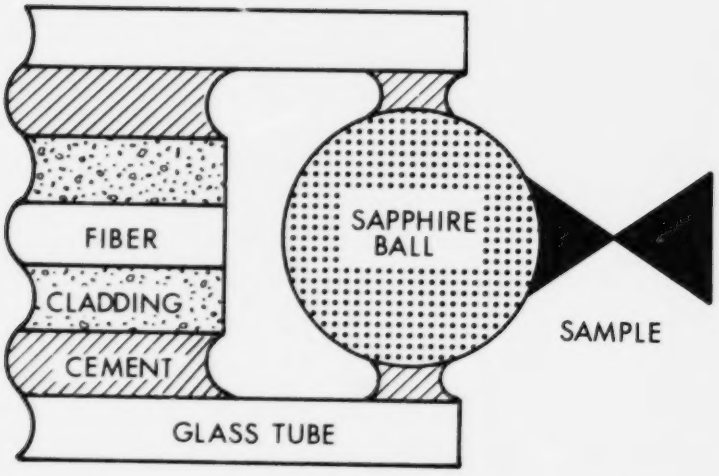


Figure 15. Schematic of ball optrode.

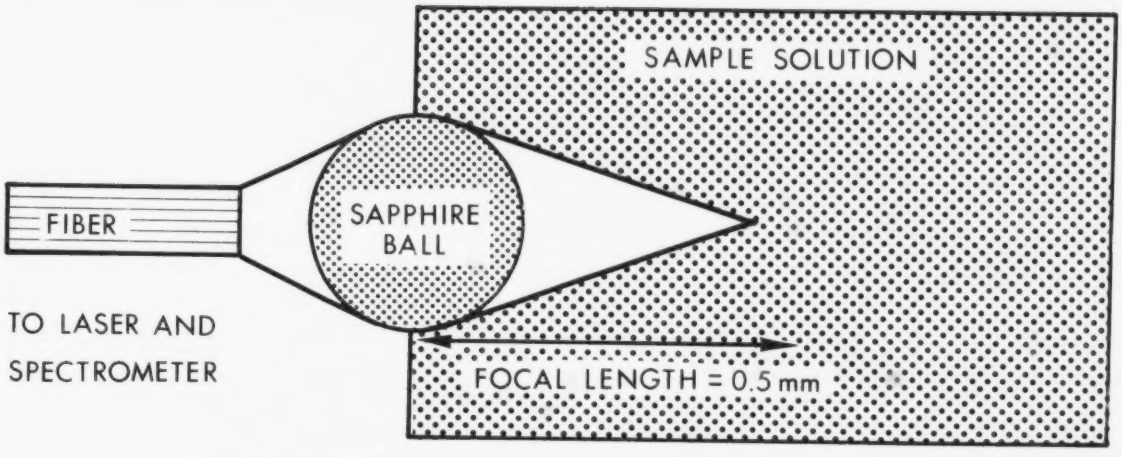


Figure 16. Field-of-view ball optrode

Figure 17. Ball optrode.

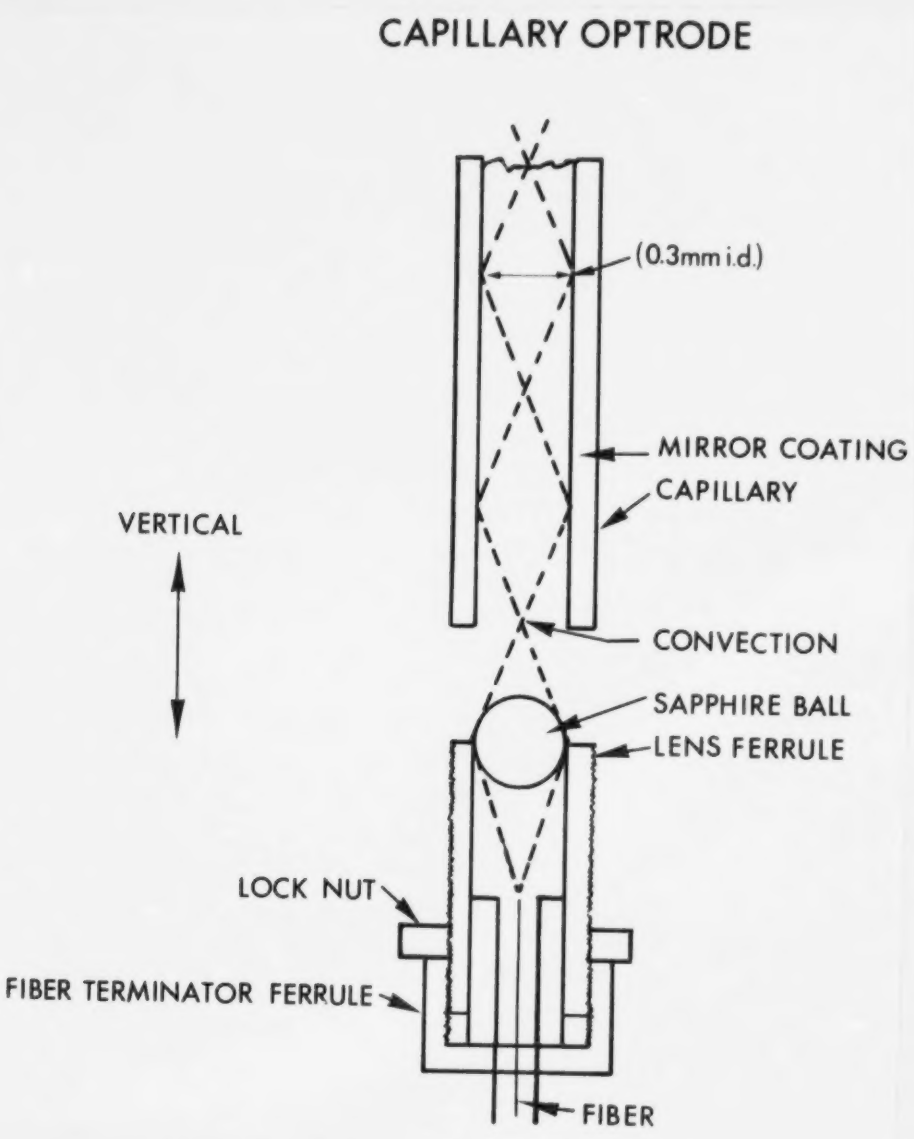


Figure 18. Schematic of capillary optrode.

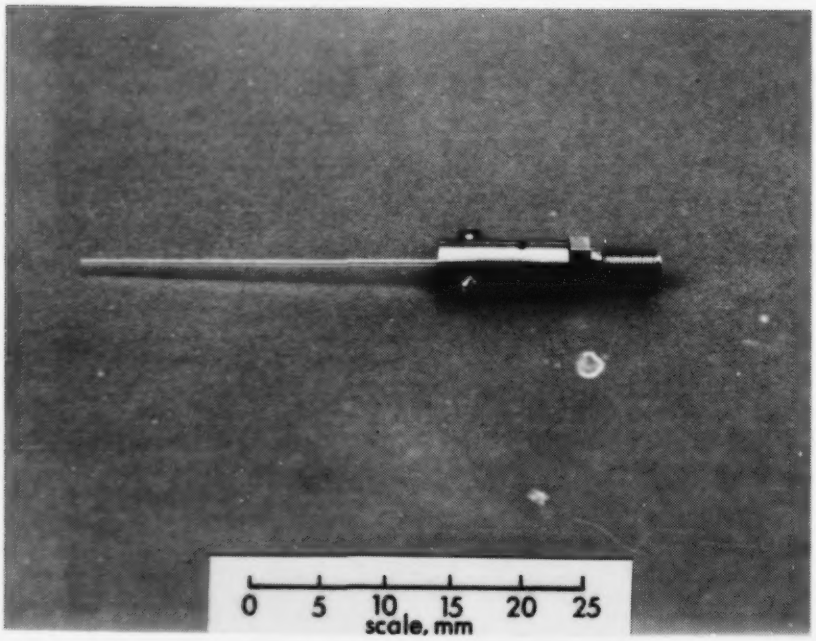


Figure 19. Capillary optrode.

great degree, the advantages of the fiber optic system. Theoretically, thermal convection driven by the laser beam (Appendix C) is an alternative. No experimental results have been gathered to support this postulation.

CHEMICALLY ACTIVE SYSTEMS

In place of the sample fiber termination, species-specific optrodes can be used. The chemical optrode is a fiber optic with a tip at its distal end. The chemical coatig is typically a fluorescent indicator or reagent which reacts reversibly with specific analytes to produce fluorescence or reduce an existing fluorescence. The optrode approach can be extended to irreversible reactions by injecting specific reagents, from a small reservoir, through a controlled microleak. Selectivity can be further enhanced by covering the tip with a semipermeable membrane.

The chemical system is considered in two parts: First, chemical reactions are chosen which specifically measure the species of interest. Second, these must be simple enough to perform reliably at the end of a fiber with reasonable reaction times and with acceptble life times. The simplest approach is to use chemically selective coatings. These coatings come in many forms such as extraction, ion exchange, and chelating resin layers; tagged antigens; and quenchable and energy transfer coatings. In systems where a reservoir is needed, water soluble or miscible reagents are used.

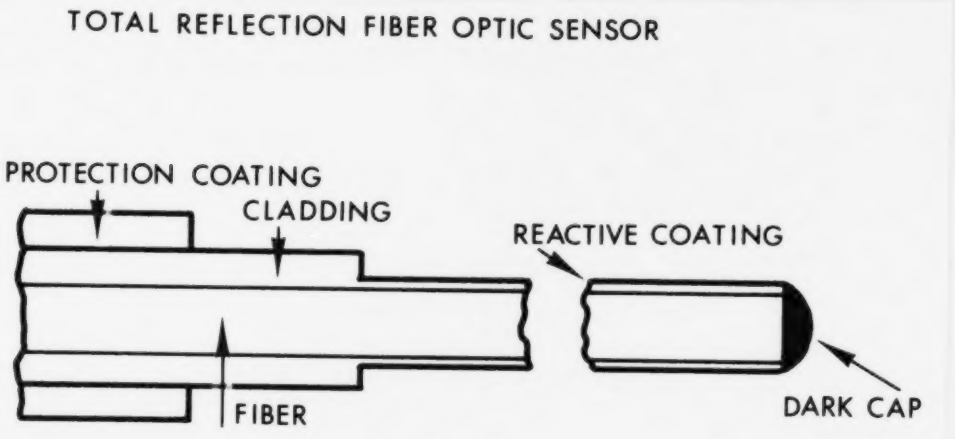
Coated Optrodes

There are two kinds of coated optrodes. The first is one in which the fiber itself is coated with the reactive reagent (Figure 20). The black cap is used to attain total reflection and, thus, increased sensitivity. In order to have effective coating, i.e., reasonable reaction times (<1 minute) and acceptable optrode lifetimes (>6 months), it is necessary to immobilize the reagent. This is done by using either polymers or gels to hold the reactive species. In many cases a special coated tip is made and then joined to the trasmit/receive fiber. Here the losses from misalignment discussed in Appendix B must be avoided.

The second type of coated optrode involves the use of a coated membrane (Figure 21). Here the reactive reagent is immobilized and placed on/within the membrane. The aqueous sample wets the membrane, reacts with the reagent, and fluoresces. The ball optrode is focused at the surface of the membrane.

Reservoir Optrodes

In cases where the reactions are not reversible and a continuous source of new reagent is needed, the reservoir optrode (Figure 22) is employed. Here the reactive reagent is on one side of a membrane and the aqueous sample on the other. The reaction takes place on and the fluorescence is emited from the surface of the membrane. The ball optrode is, once again, focused on the membrane surface (Figure 23). The usage rate of reagent is approximately 1 ml/mo making long-lived optrodes practical.



Firgure 20. Schematic of coated optrode.

Figure 21. Coated membrane optrode.

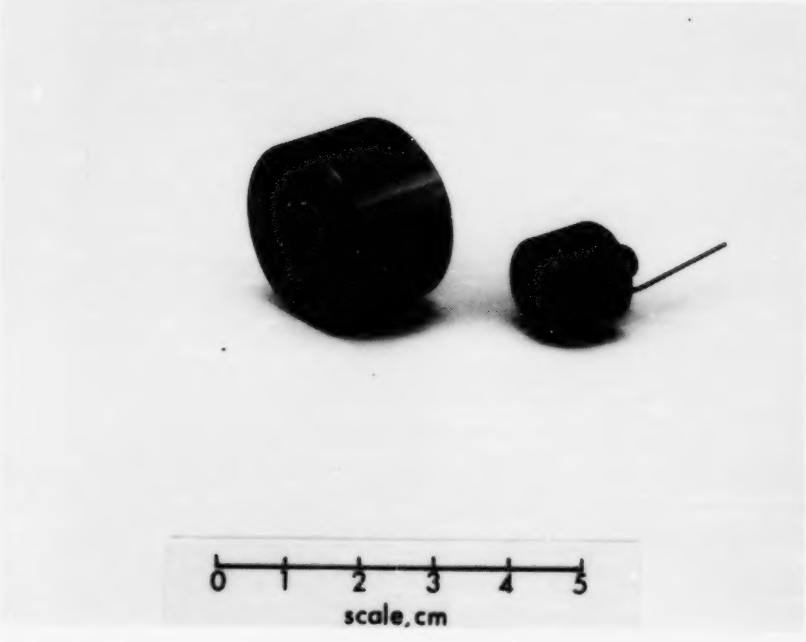


Figure 22. Reservoir optrode.

CONTINUOUS SENSING OPTRODE

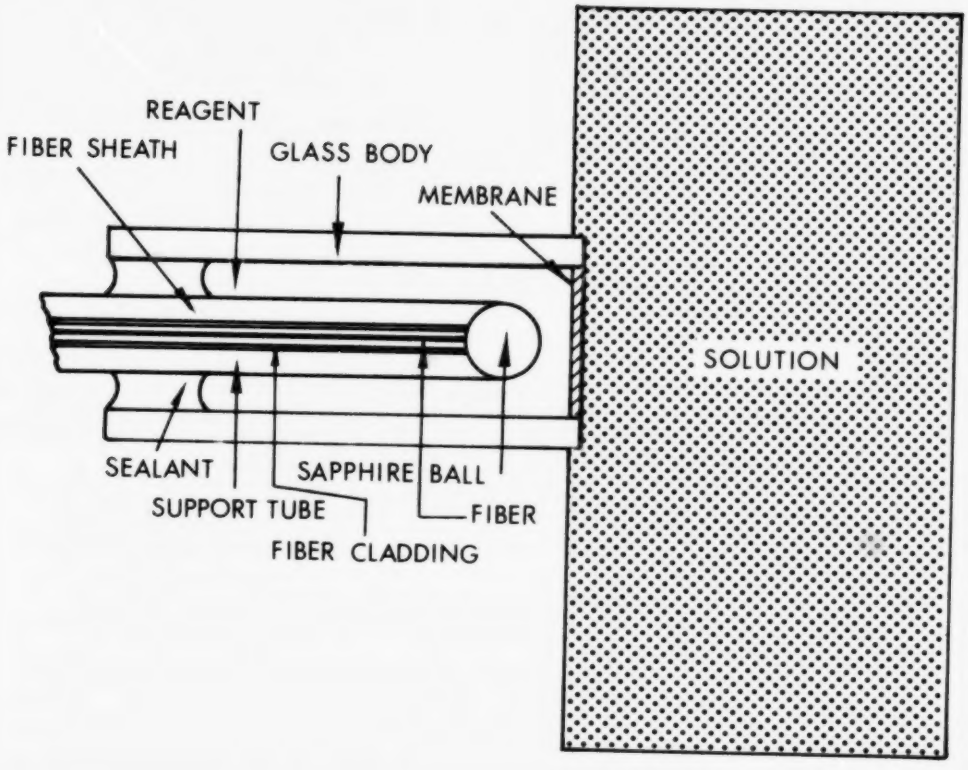


Figure 23. Schematic of reservoir optrode.

Self-Cleaning Optrodes

In the analysis of groundwater or drinking water there is always the chance that the sample will contain particulate matter which could contaminate or clog the optrode. To be prepared for such a possibility, a self-cleaning optrode was designed in which the thermal characteristics of the laser beam are used to form a sessile bubble (Figure 24) which can either be used to protect the optrode or to push the sample away from it.

It must be noted that the optrode has no "magical" analytical capabilities. Any measurements that can be made with an optrode, can be performed better under laboratory conditions.

At present there are no completely engineered optrodes. Breadboard systems exist for uranium, plutonium, iron, europium, tracers (organic dyes), temperature, pressure, and pH. Optrodes currently being researched include americium, inorganic chloride, organic chloride, copper, alcohols, aldehydes, iodine, sulfate, cyanide and Eh. Two optrodes for detecting H_2S and O_2 gas are also being worked on. Sensitivities depend on the available fluorescent reactions. Generally, detection limits range from 10 ppm to 10 ppb at 500 m distances.

SELF CLEANING OPTRODE

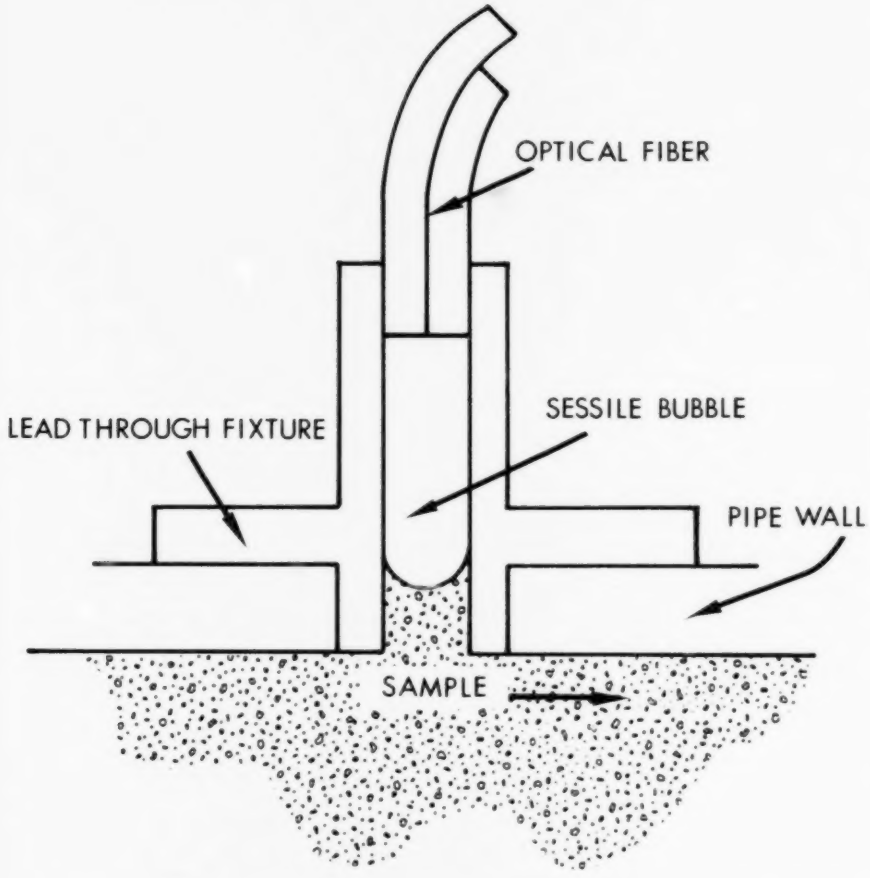


Figure 24. Schematic of self-cleaning optrode.

SECTION 6

SUMMARY OF EXPERIMENTAL RESULTS

There have been considerable data collected on the performance of the remote fiber optics spectrometer systems. These data relate both to the behavior of the fibers per se as well as the total analytical device.

FIBER PROPERTIES

Two properties of the optical fibers limit the sensitivity of the analytical system-transmission efficiency and input power limitations.

The distance between the sample and the analyzer are dictated by the amount of signal that reaches the detector. This depends on how much irradiation energy is lost between the laser and the sample as well as how much fluorescence light is lost between the sample and the detector. Table 1 summarizes the loss of energy as a function of distance for a typical glass fiber transmitting visible radiation. From a spectroscopic point of view the losses over the fiber can be compensated for by increasing the laser input power. When fibers are used, however, there is a limit to their power-handling capability (Figure 25). There is also a practical limit to the size laser that can be used in a mobile device.

TABLE 1. TRANSMISSION EFFICIENCY VS. DISTANCE (40 db/km LOSS)

Distance (meters)	Transmission (%)
0	100
50	63
100	40
150	25
200	16
500	1
1000	0.01

SAMPLE CHARACTERISTICS

The fiber optic method is designed to operate with aqueous systems. The species to be measured is in solution, at least until it interacts with a chemical optrode, if need be.

The three concerns about the sample are its opacity, whether or not there are particles present, and the possiblity of salts precipitating out. Normally a 5 mm sample depth is desired (Figure 26) although measurements have been made where the depth of view has been as small as a few microns to as large as many centimeters. It is rare that dirty (murky) water will be opaque in the few micron thickness range.

Particulates are no problem as long as they do not add a fluorescent or scintillation background. There are many ways to assure that they are kept away from or removed from the optrode.

Dissolved salts, which may precipitate out and coat the fiber may be a potential problem, particularly in the case of high ferrous ion concentrations under oxic conditions. This situation, however, is not sufficiently common in groundwater to pose a threat to the usefulness of the optrode and fiber optics. Self-cleaning optrodes are a possible solution to this potential problem.

CHEMICAL ANALYSES

During the initial part of this research the possibility of analyzing several chemical species was investigated. A great deal of information was accumulated, processed, and analyzed. The results of this effort have been summarized for this report and representative data are presented.

Inorganic Chloride

The inorganic chloride (Cl^-) optrode is of the coated membrane design. It is designed around the reaction of Cl^- with silver fluoresceinate to yield a fluoroescence signal. Silver binds fluorescein so that it does not fluoresce. When Cl^- is present, however, the preferred reaction is the formation of the AgCl precipitate with the release of the highly fluorescent fluorescein. The fluorescence intensity is a direct measure of how much silver has reacted with the Cl^- and this, in turn, is proportional to the Cl^- concentrations.

The Cl^- optrode has been perfected in the higher concentration ranges (10^{-3} to 10^{-4} M Cl^-). The experimental results for this work are shown in Figure 27. It should be noted that at 10^{-3} M the Cl^- optrode gives over 1 x 10^5 counts per second (cps). Experience has shown that as the concentrations go lower, a plot of molarity vs. count rate should tend to linearity, and the slope of the curve should diminish. This extrapolation to detectable Cl^- concentrations in the sub parts-per-million range appears realistic. In practice, however, there are several considerations that preclude this simple

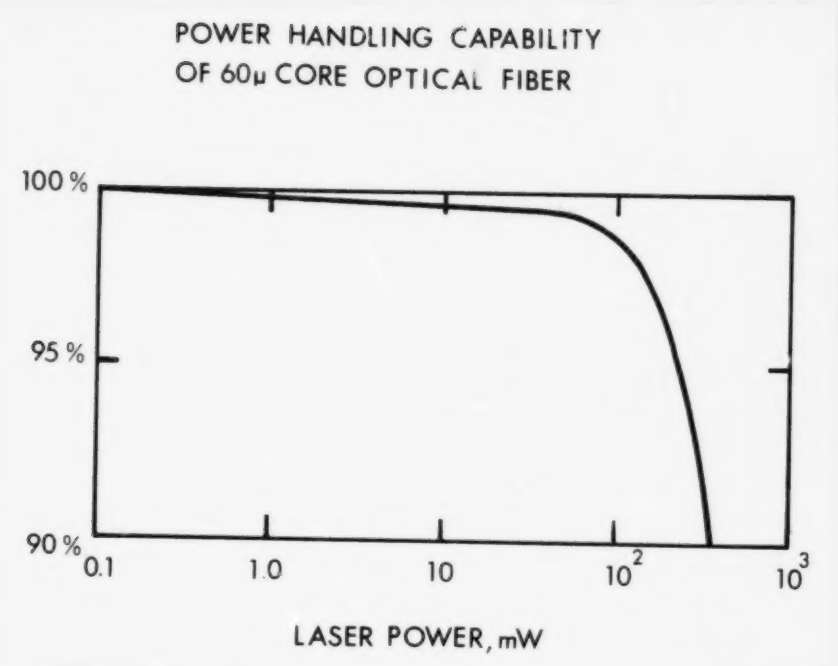


Figure 25. Power-handling capability of 60 μm optical fiber.

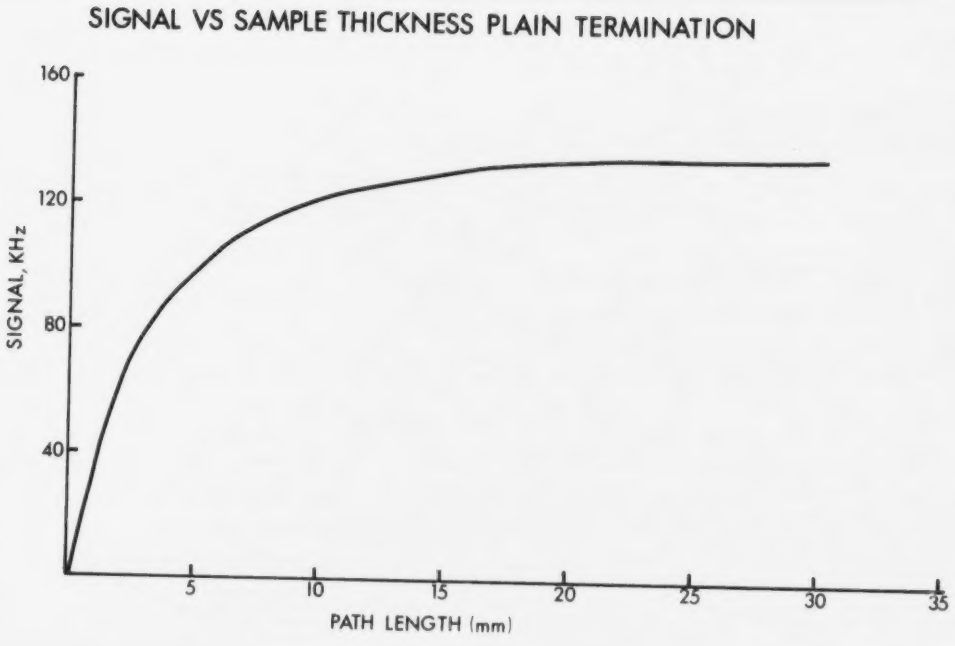


Figure 26. Signal vs. sample depth.

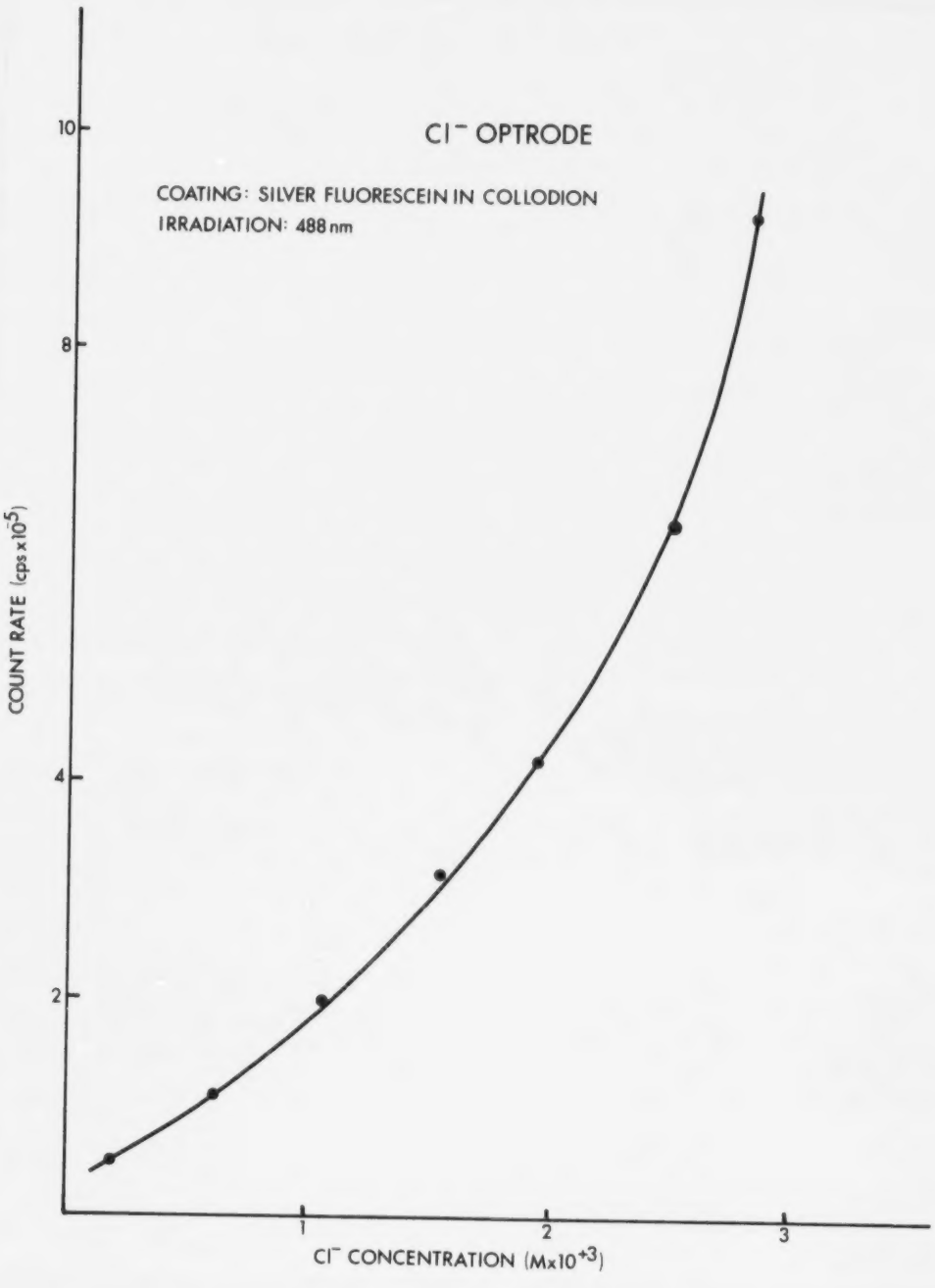


Figure 27. Calibration of Cl- optrode.

extension of the data:

(a) The type of silver fluoresceinate coatings, and

(b) The effect of low concentrations on chemical equilibrium, solubilities, reaction rates, and reaction efficiencies.

The immobilization of the silver fluorescinate appears to be the key to ultrasensitive repeatable measurements. The preparation of uniform silver fluoresceinate coatings in which the reactive agent is readily accessible to the Cl^- is needed. The data shown in Figure 27 was obtained for the silver fluoresceinate immobilized in collodion. Greater sensitivities (10^{-5} to 10^{-6} M) have been attained using a polymer substrate in whose intersticies the fluoresceinate is retained, but these coatings cannot be made uniform and the data are inconsistent. Theoretically, when a good host material is found for immobilizing silver fluoresceinate, then Cl^- detection should approach that of fluorescein (Figure 28). In practice, however, the solubility of AgCl is limiting but sensitivities to 10 ppb seem reasonable.

Organic Chloride

The organic chloride work is presently focusing on a two-step process. The first reaction is the conversion of organic chloride to Cl^- by oxidation. The second step is the Cl^-, silver fluoresceinate reaction discussed previously. For oxidizers, such reagents as immobilized (polymer-bound) CrO_3 complexes, $KMnO_4$ held in crown complexes incorporated in polymers, or singlet oxygen produced by light from appropriate immobilized colored materials (which are either resistant or present in large excess, depending on the dye type) have been considered. CrO_3, immobilized on "Selectite" resin is presently the choice of oxidizer. No attempt is made to control the oxidizing strength of the CrO_3, and it is now assumed that total oxidation of the organic chloride takes place. Preliminary measurements on this system indicate that the CrO_3 reaction is well behaved and predictable making quantitative results possible.

One problem that must be solved if this optrode is to work in the field is that of distinguishing the Cl^- produced by oxidation of organic chloride from that Cl^- normally present in the groundwater. The most direct approach is to surround the immobilized CrO_3-silver fluorescein optrode with a semipermeable membrane which passes only organic chloride, thus excluding the normal Cl^- in the system. Three reactions, therefore, take place at the optrode:

(a) Exclusion of normally present Cl^- by use of a selective membrane,

(b) Oxidation of the organic chloride to Cl^- by CrO_3,

(c) Detection of Cl^- (and thus organic chloride concentration) by silver fluoresceinate.

By using a much weaker oxidizing reagent, less stable chlorinated organics can be detected. Two highly unstable ones that can be readily selected for are chloroform and vinyl chloride. Here selectivity can be enhanced by using an optrode pair with different oxidizers.

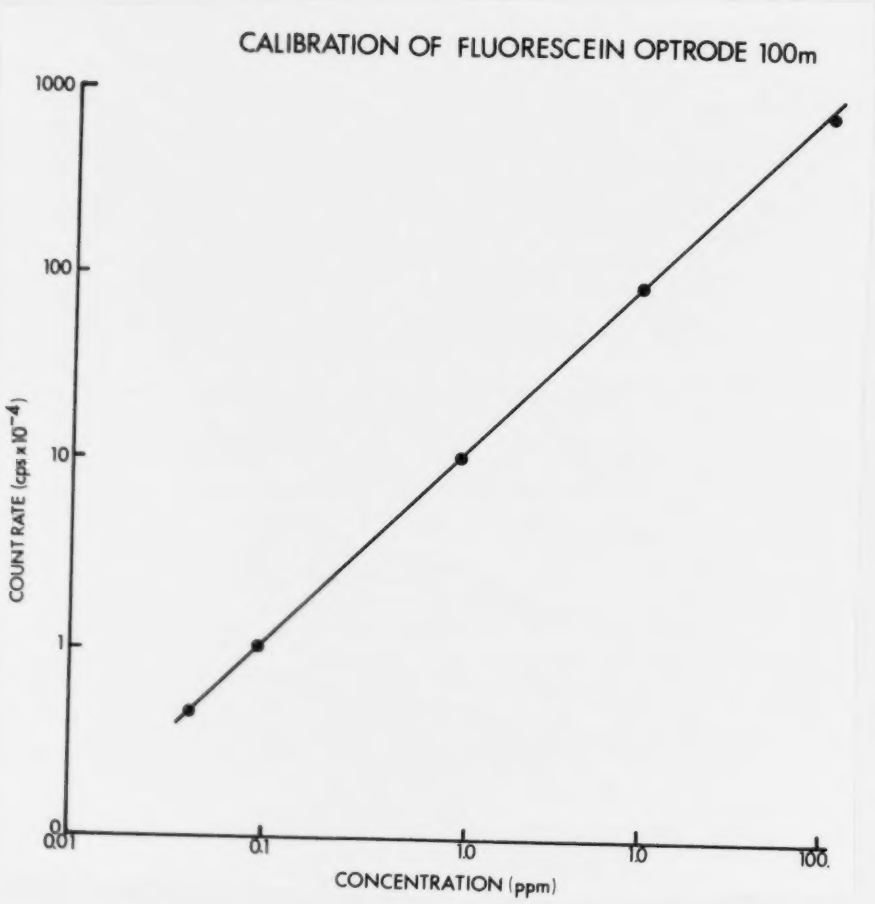


Figure 28. Calibration of fluorescein optrode.

Aldehydes

Schiff reagents, which are normally fluorescent, are quenched when reacted with aldehydes. Qualitative measurements, using a Schiff reagent based on acriflavin, show a reduction in fluorescence as a function of aldehyde content. No quantitative work has been done.

A semipermeable membrane in front of the fiber tip can discriminate in favor of the small formaldehyde molecule over all other aldehydes. If this discrimination is not complete for a few other aldehydes (notably acetaldehyde), a pair of optrodes with and without this membrane is best used. This second optrode can be either a guard channel or allow calculation to separate the formaldehyde signal from other aldehydes present.

It is possible to make the Schiff reaction reversible by having a slightly acidic medium around the fiber tip. This extends the life of the optrode and makes it possible to do continuous, long-term monitoring for these substances.

Alcohols

Alcohols resemble water in many ways and, therefore, direct measurements are impossible. The use of derivatives is limited and not suitable for optrode implementation. The best approach is to selectively oxidize the alcohols to aldehydes (specific oxidizers such as chromic oxide-pyridine complexes are available for this conversion) and then use a Schiff reagent. The oxidizer can be dissolved in the medium between the membrane and the fiber tip to make the fiber an alcohol detector. To prevent the exhaustion of the reagent, which would limit the optrode lifetime, a reservoir must be provided around the reaction gap between the fiber tip and the small-area membrane. A reservoir of 10 ml has been calculated to be adequate. If both aldehydes and alcohols are present, two optrodes in series can be used -- the first to measure aldehydes and the second the alcohols -- if it is assumed all the aldehydes are used up at the first site. No experimental work has been done to date on the mixed systems.

Sulfates

$SO_4^{=}$ has been given a cursory look. The present approach is to coat an optrode with immobilized barium chloranilate (the barium salt of chloranilic acid) and let it react with the $SO_4^{=}$. The barium quenches the fluoroescence of the chloranilic acid. When $SO_4^{=}$ is present, the barium preferentially attaches to the $SO_4^{=}$ freeing the acid so it can fluoresce. The intensity of the fluorescence is, therefore, a direct measure of the amount of barium released which in turn can be directly related to $SO_4^{=}$ concentration. Although preliminary work indicates that this technique will work, there is concern about the ability to reach sensitivities of 1 ppm or below. One reason is that the "very insoluble" barium sulfate is really soluble at 27 ppm and this drives back the reaction equilibrium and reduces sensitivity. Extant data is at 100-1000 ppm. This must be tested experimentally at the lower concentrations to determine sensitivity limits.

Nitrates

No work has been done on nitrates. It is planned to use a two-step reaction to measure this anion. The nitrate is first reduced to nitrite using hydrazine sulfate, and the resulting nitrite, in the presence of acid, will quench the fluorescence of an amine as it is converted to a diazo compound. A simple reservoir can be used so that both reactions occur immediately in sequence.

Uranium

Although uranium is not specifically called out in this program, results are included because of EPA's potential involvement in the environmental aspects of nuclear waste burial sites.

The uranium data give excellent examples of the advantages of optrodes. In Figure 29 (spectrum 2) it can be seen that 10^{-5} M of UO_2^{+2} in water gives little or no signal. If a reservoir optrode is used, however, and 1 percent phosphoric acid is injected into the system, 10^{-5} M UO_2^{+2} is detectable with an exceptionally good signal to noise (sepctrum 3). Two percent phosphoric acid, however, is too much and reduces the signal (spectrum 5) while 1 percent nitric acid helps very little (spectrum 6). The spectrum for 1 ppm uranium, using a phosphoric acid reservoir optrode, appears in Figure 30.

Pesticides

The objective when looking at a fiber optic technique to detect organophosphates (pesticides) was to develop a method whereby a single optrode would suffice for detection and quantification. Evaluation of the natural fluorescence of the materials indicated that no single optrode will cover the range of compounds to be monitored. Some pesticides, e.g., Guthion, Parathion, and Malathion have strong fluorescence spectra spread over a wide spectra range. Other compounds must still be investigated. Most carbamate-based pesticides also have strong, individual characteristic fluoresences. In general, no difficulties are expected in developing fiber optric techniques for pesticide detection and identification. Here the question is the number of optrodes needed to cover all pesticies of interest to EPA.

A more general way to detect organophosphorous compounds, and other compounds with the same toxic properties, is to group them by their biological effect; i.e., these compounds are cholinesterase inhibitors. Using this approach it is possible to measure a whole class of dangerous species with a single fiber system. The present research has, therefore, focused on an optrode for organophosphorous based on an enzymatic test where the inhibition of cholinesterase acting on fluorogenic choline ester is used. Here a non-fluorescent choline ester, but whose hydrolysis products are fluorescent, is reacted for a known time with a fixed cholinesterase concentration and the resultant fluorescent level measured. The presence of inhibitors for this enzyme (which is the physiological basis of pesticide activity) will retard this reaction and reduce the fluorescence. The fluorescence is referenced to the Raman backscattering due to the fiber itself, thus normalizing out source, detector, spectral sorter, and systems fluctuations.

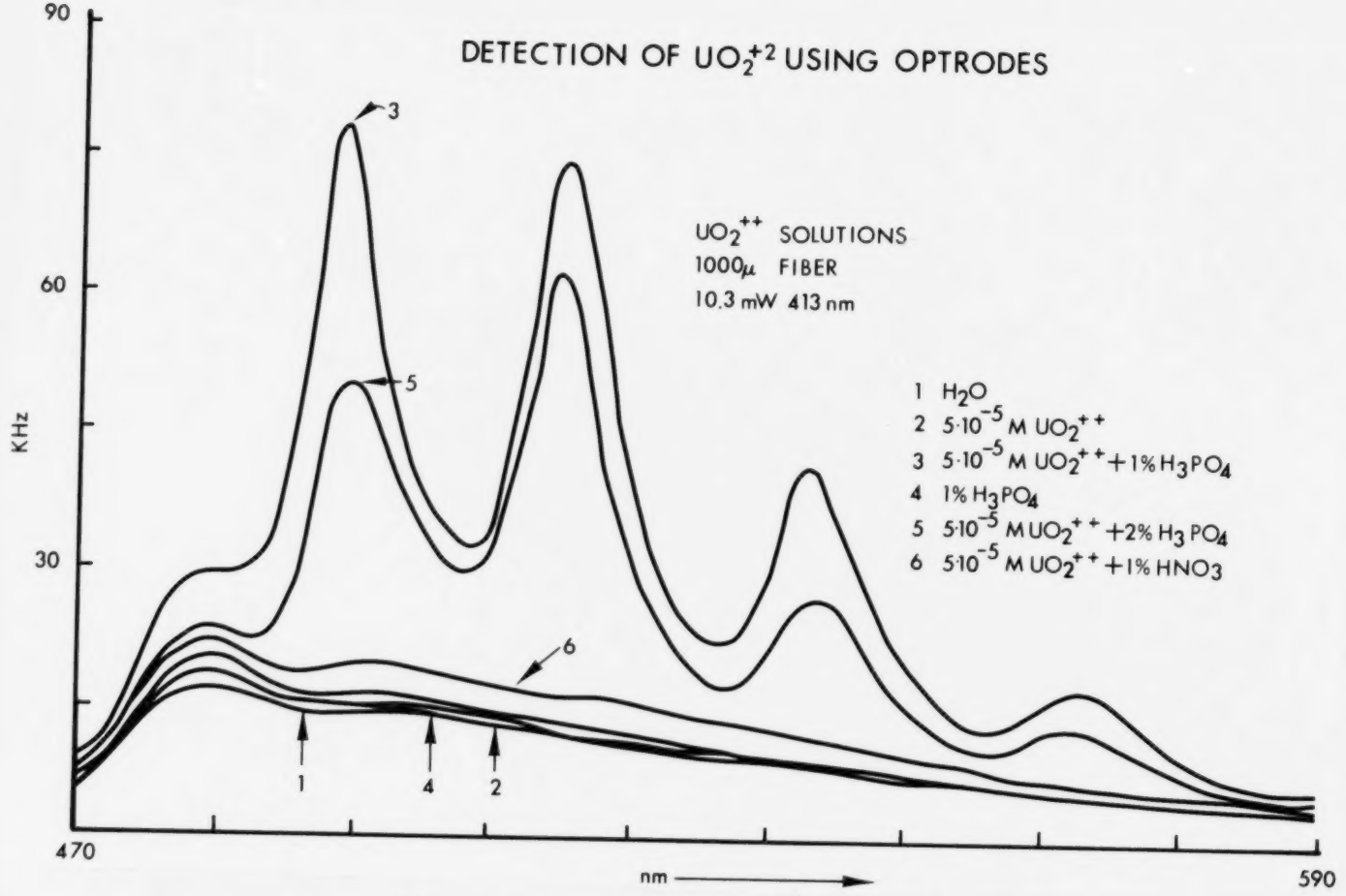


Figure 29. Detection of UO_2^{+2} using optrodes.

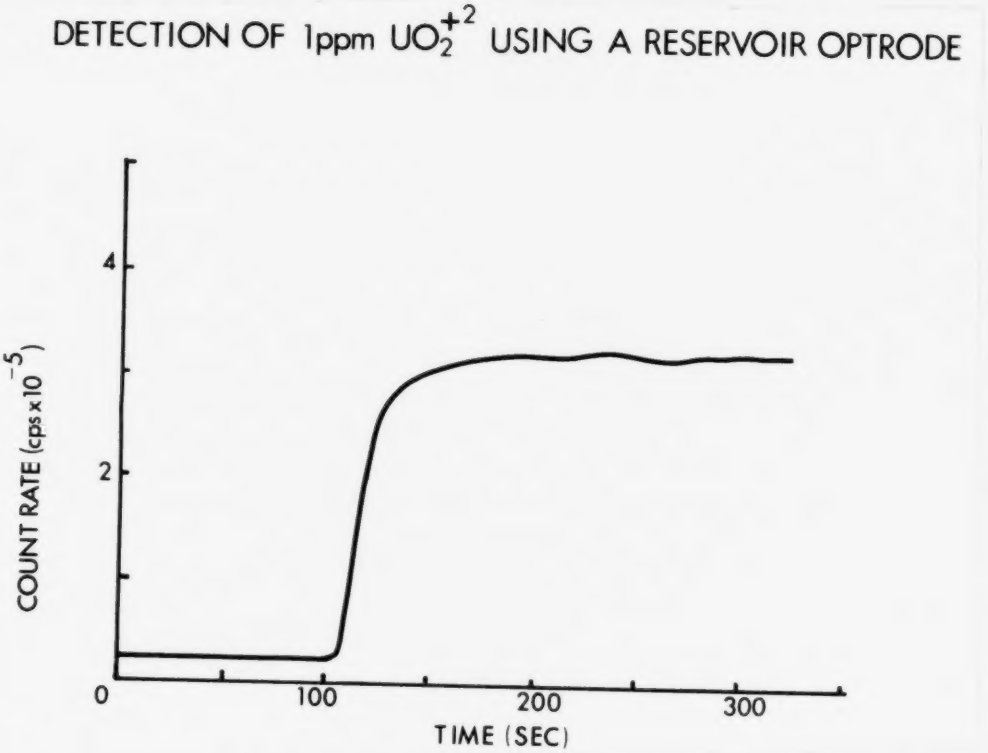


Figure 30. Detection of 1 ppm UO_2^{+2} at 100 m.

Figure 31 shows an oversize view of a possible organophosphorous optrode configuration. Here a small vial of stabilized, preserved enzyme solution is internally presurred by a small amount of Freon. The flow rate for the enzyme solution (approximately 10^{-7} ml/s) is controlled by a small leak and the Freon overpressure. Flows of this magnitude assure a long-lived optrode. The enzyme solution flows through a porous capillary tube which is coiled around a central cylinder. If pesticide is present, they enter the system through the capillary and react with the enzyme. The top one-third of the central cylinder is filled with bonded liquid chromatography packing which has been presaturated with the fluorogenic substrate. This is followed by a filter and a sensing zone into which the fiber optic is plugged.

For calibration the total fluorescence per unit observation time is determined with no inhibitor present and then as a function of inhibitor concentration. The calibration curve will show a negative slope with maximum fluorescence when no pesticide is present.

The total optrode package, as presently envisioned, would be 2 cm in diameter and 10 cm long.

Although enzymatic reactions are probably the most desirable long-term approach, the optrode needed to do the detection is quite complex as shown in Figure 31. For the short term, therefore, it may be necessary to return to the multiple fiber concept and measure the characteristic fluorescence from various classes/types of pesticides.

TRACER DETECTION

The use of tracers in groundwater studies is universal. EPA can use tracers to identify polluting sources and to determine the route of species as they travel through the groundwater.

Several tracer materials were tested as shown in Table 2. These results were obtained using a simple fiber optic (Figure 12). Increased sensitivity is attainable by using optrodes. It should be noted that although the majority of tracer compounds are organic dyes, rare earth compounds also make reasonable tracers, especially for studies related to nuclear waste transport in groundwaters. The signal level from 10 ppb Rhodamine 6G at 100 m is shown in Figure 32.

PHYSICAL MEASUREMENTS

Physical transducers are used whose outputs are light signals which can be transmitted through the fibers. These signals can be simple changes in light intensity or have spectral dependence as well.

TOXIC ORGANOPHOSPHATES SENSOR OPTRODE

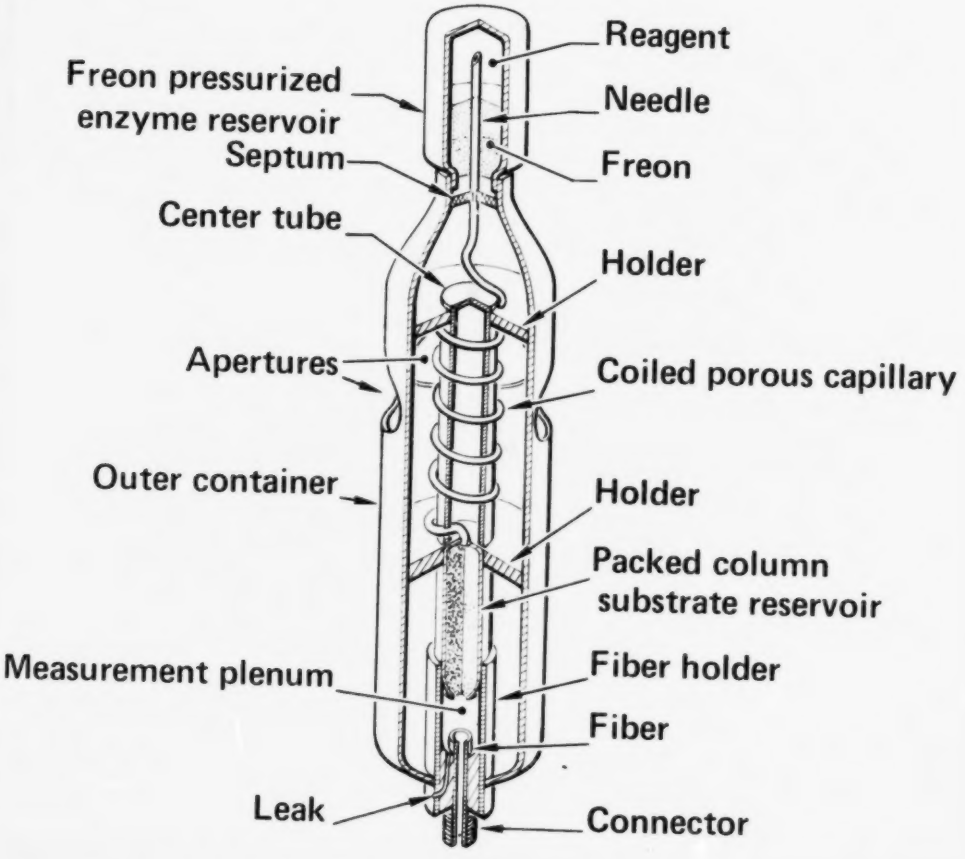


Figure 31. Organophosphorous optrode.

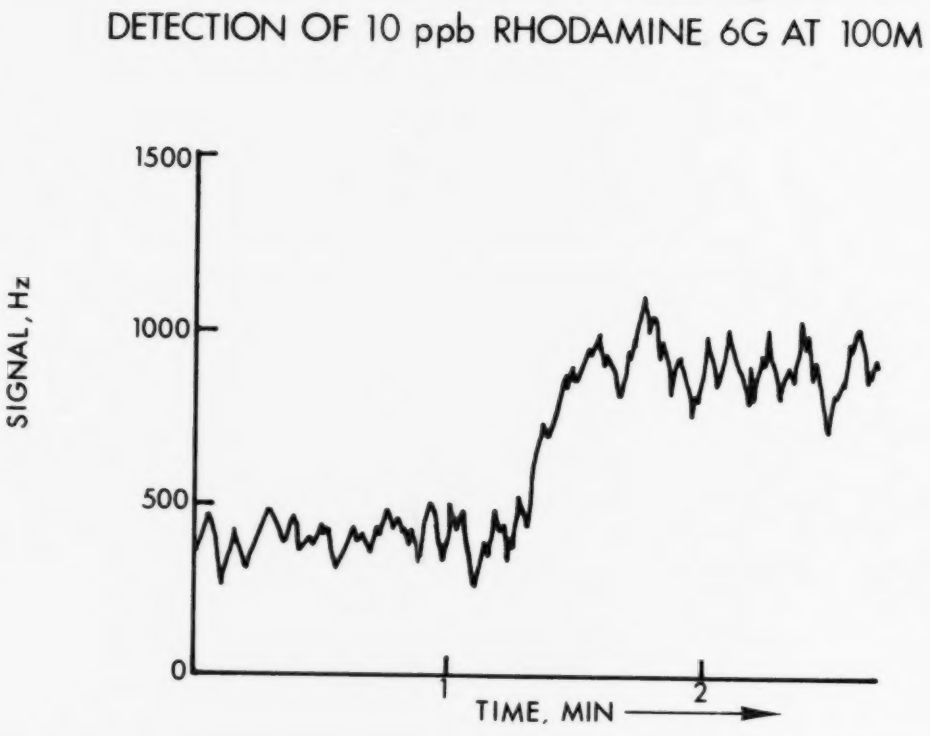


Figure 32. Detection of 10 ppb rhodamine 6G at 100 m.

TABLE 2. SIGNAL INTENSITIES FOR 1 ppm OF TRACER COMPOUNDS AT 100 m USING RFF

Tacer Compound	Signal (cps x 10^{-4})
Rhodamine 6G	50
Rhodamine G	40
Brilliant Sulphoflavine	20
Fluorescein	20
Terbium nitrate	10
Europium nitrate	9
Dichlorofluorescein	9
Acridine Red	9
3,3'Diethyloxodicarbo cyanine iodine	5
Th-1-Amino-4-hydroxylanthraquinoine	1

Temperature

Several temperature optrodes have been investigated. Here the principle of operation is changes in the intensity of the spectral lines of glasses as a function of temperature. Temperature information may be gleaned by observing the behavior of a single line or by ratioing two lines. A general schematic of a temperature optrode is shown in Figure 33. Comments on the glass tip are shown in Figure 34. An optrode has been constructed based on ruby temperature dependence (Figure 35). Here the tip of a quartz fiber is converted to ruby by exposing it to chromium oxide vapors. The effect of temperature on the ruby spectrum is shown in Figure 36.

Calibration (Figure 37) is accomplished by plotting the ratio of the two spectral peaks. In a similar manner neodynium (Nd) and chromium (Cr) doped glasses (Figure 38) can be used for temperature optrodes. Work has also been done using europium (Eu) and samarium (Sm).

The temperature optrodes either cover large temperature ranges with moderate temperature resolution (0.1°C) or narrower spans with higher accuracy (0.01°C). Optrodes with steep spectral slopes vs. temperature give the best resolution.

Pressure

The pressure optrode uses a bellows arrangement (Figure 39) in which the extension or contration of the bellows determines the light intensity reaching the detector. The ball optrode (Figure 40) is focused onto a fixed mirror or fluorescent spot. At standard temperature and pressure (STP) the mirror (or spot) are at the focal point of the ball. Thus the laser light which impinges

SCHEMATIC TEMPERATURE OPTRODE

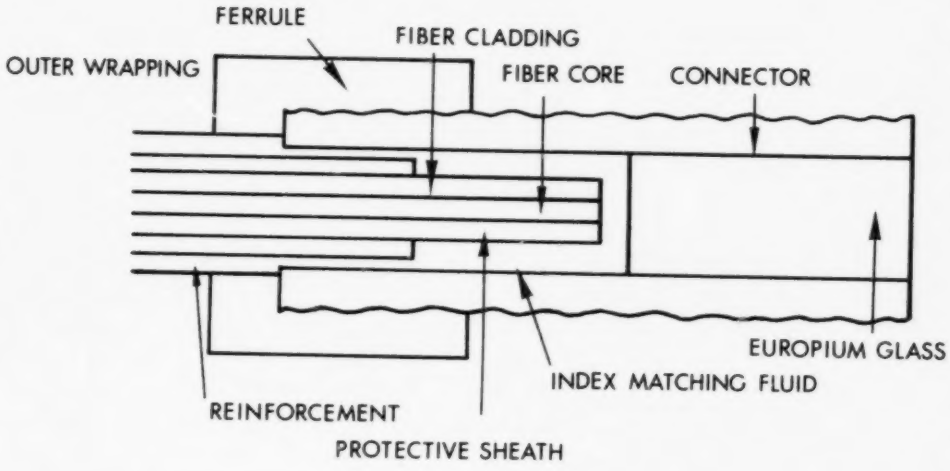


Figure 33. Schematic of temperature optrode.

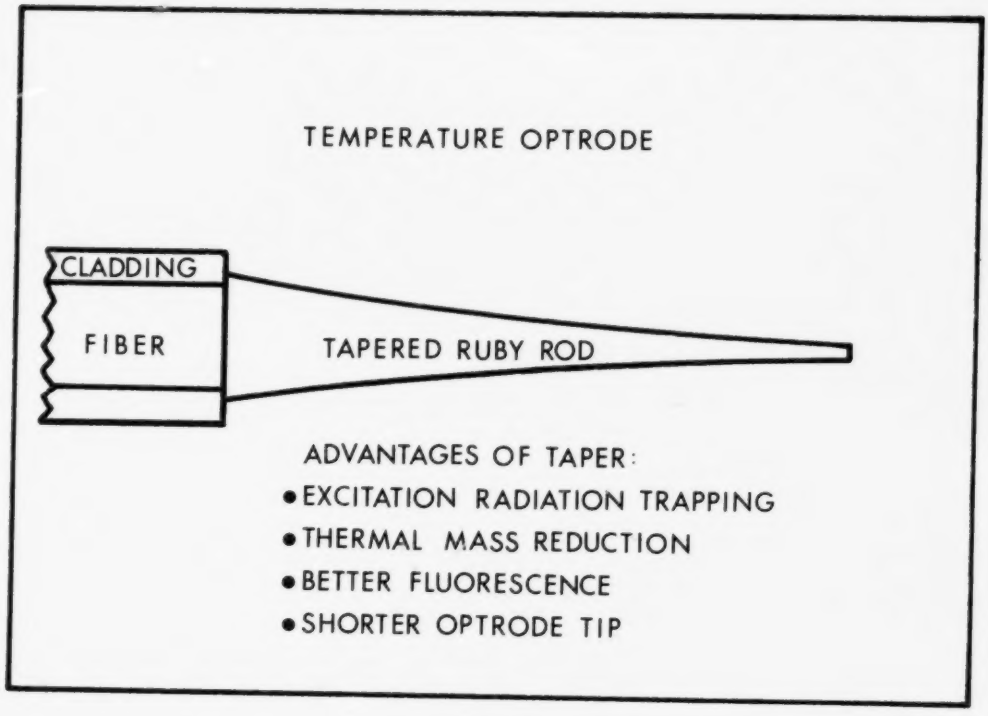


Figure 34. Temperature optrode tip.

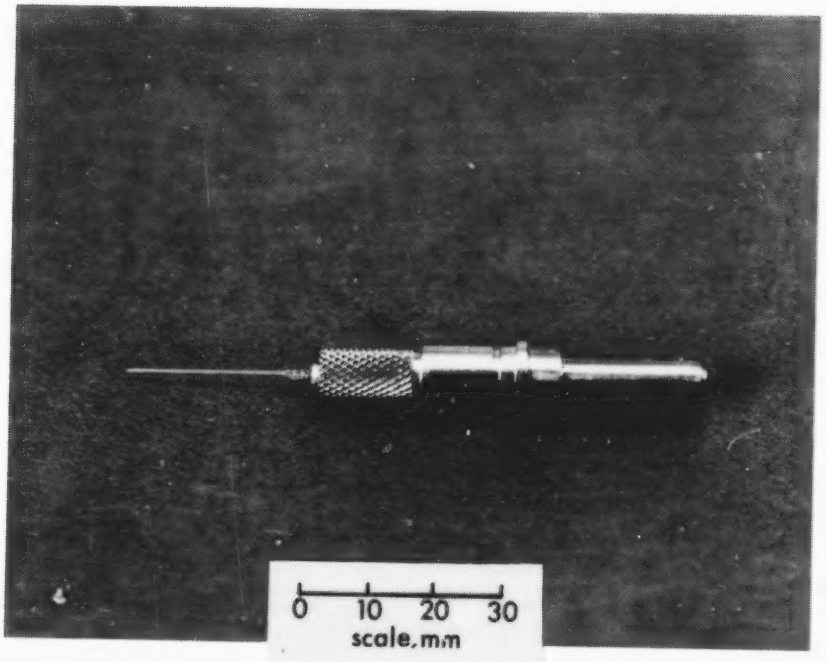


Figure 35. Temperature optrode.

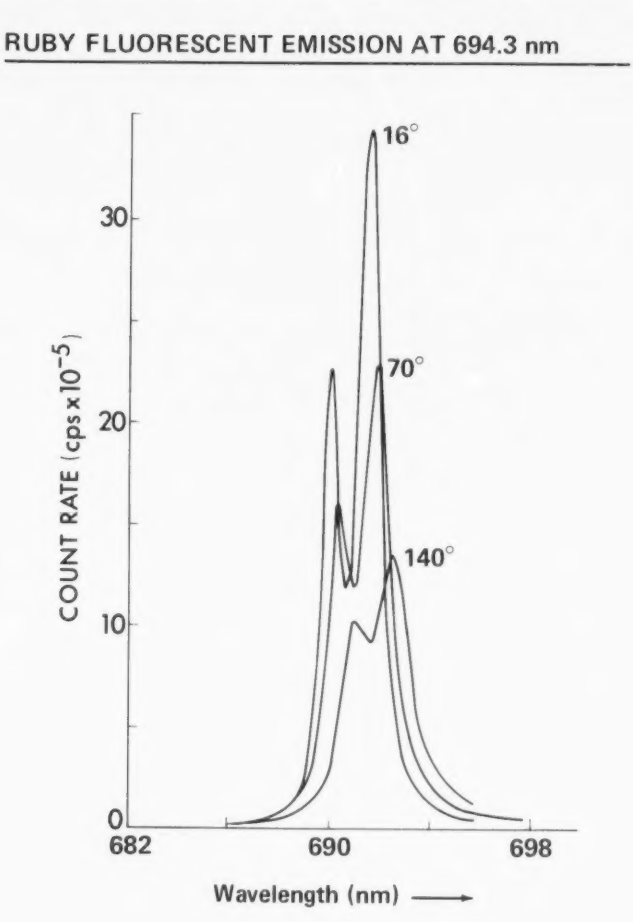


Figure 36. Temperature dependence of ruby spectral response.

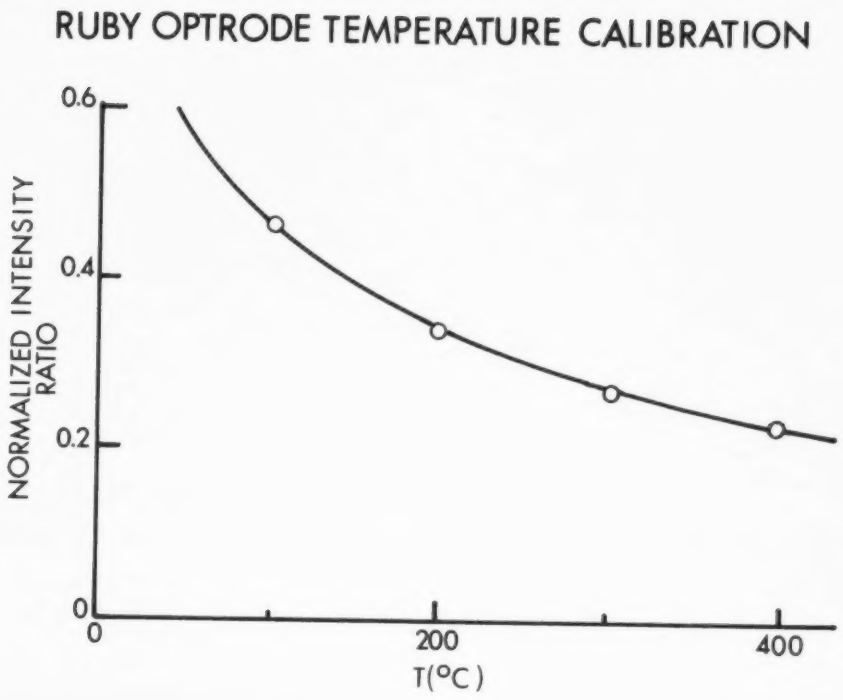


Figure 37. Calibration of ruby temperature optrode.

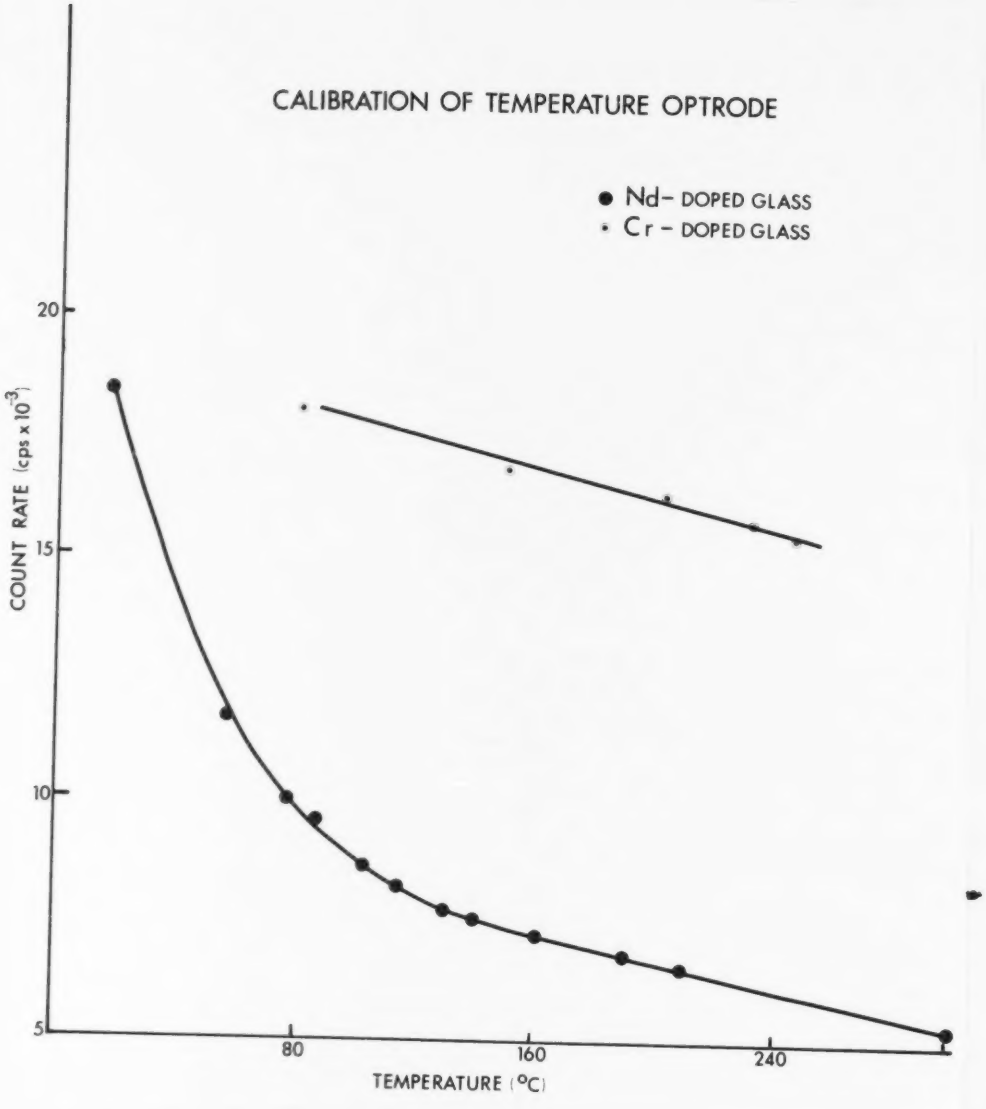


Figure 38. Calibration of Nd and Cr glass optrodes.

SCHEMATIC PRESSURE OPTRODE

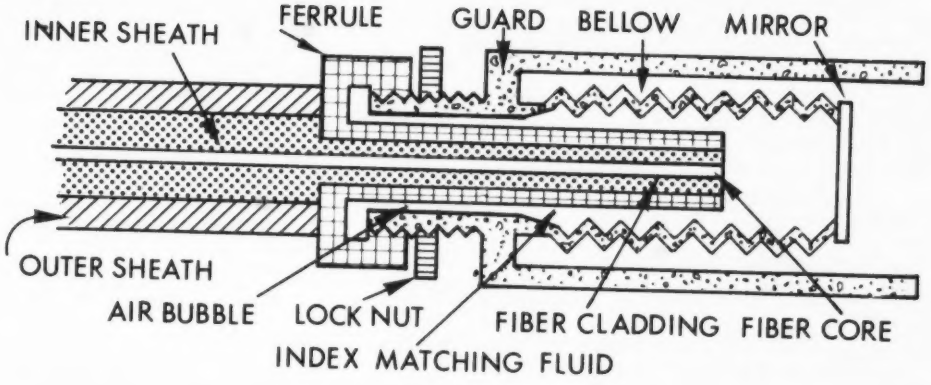


Figure 39. Schematic of pressure optrode.

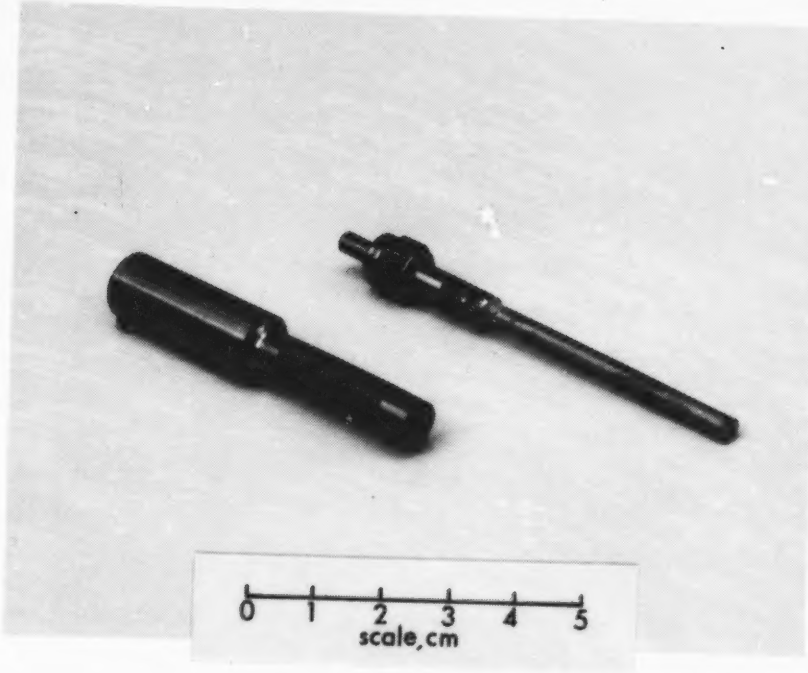


Figure 40. Pressure optrode.

on the mirror (or spot) gives the greatest signal at the detector. If the pressure changes, however, the mirror (or spot) is no longer in focus and the light intensity drops. Measurements of increased or decreased pressure can be made. A typical calibration curve is shown in Figure 41. Resolution is presently of the order of 0.01 lb/in^2 and is dependent on the distance the bellows moves as a function of pressure. The pressure range and resolution, therefore, is selectable within the limits imposed by bellows characteristics.

pH

There are numerous fluorescent indicator dyes whose fluorescence turns off and on over selected pH ranges. These dyes are immobilized in a porous matrix and indicate pH by changes in their signal intensity. It usually takes several dyes to cover a broad pH range. Those dyes which cover a broad range, do not give good resolution.

Three of the dyes studied were acridine orange, fluorescein, and neutral acriflavine. The pH dependence of acridine orange is shown in Figure 42. As can be seen from this spectrum there is room for many pH resolution elements between pH 7.0 and 9.5. The pH dependence of fluorescein is shown in Figure 43. Figure 44 is a calibration curve for a pH optrode using neutral acriflavine.

Eh

There are a series of fluorescent triarylmethane and triazinyl dyes which loose their fluorescence at selected redox potentials. A preliminary evaluation of the number of Eh dependent dyes and other couples which are available indicates that the Eh range between 1.1 and -0.6 V can be covered in 0.1 V increments. Unfortunately, many optrodes would be required to accomplish this. Only preliminary experiments have been undertaken and these are inconclusive as to the overall potential of the optrode to measure Eh.

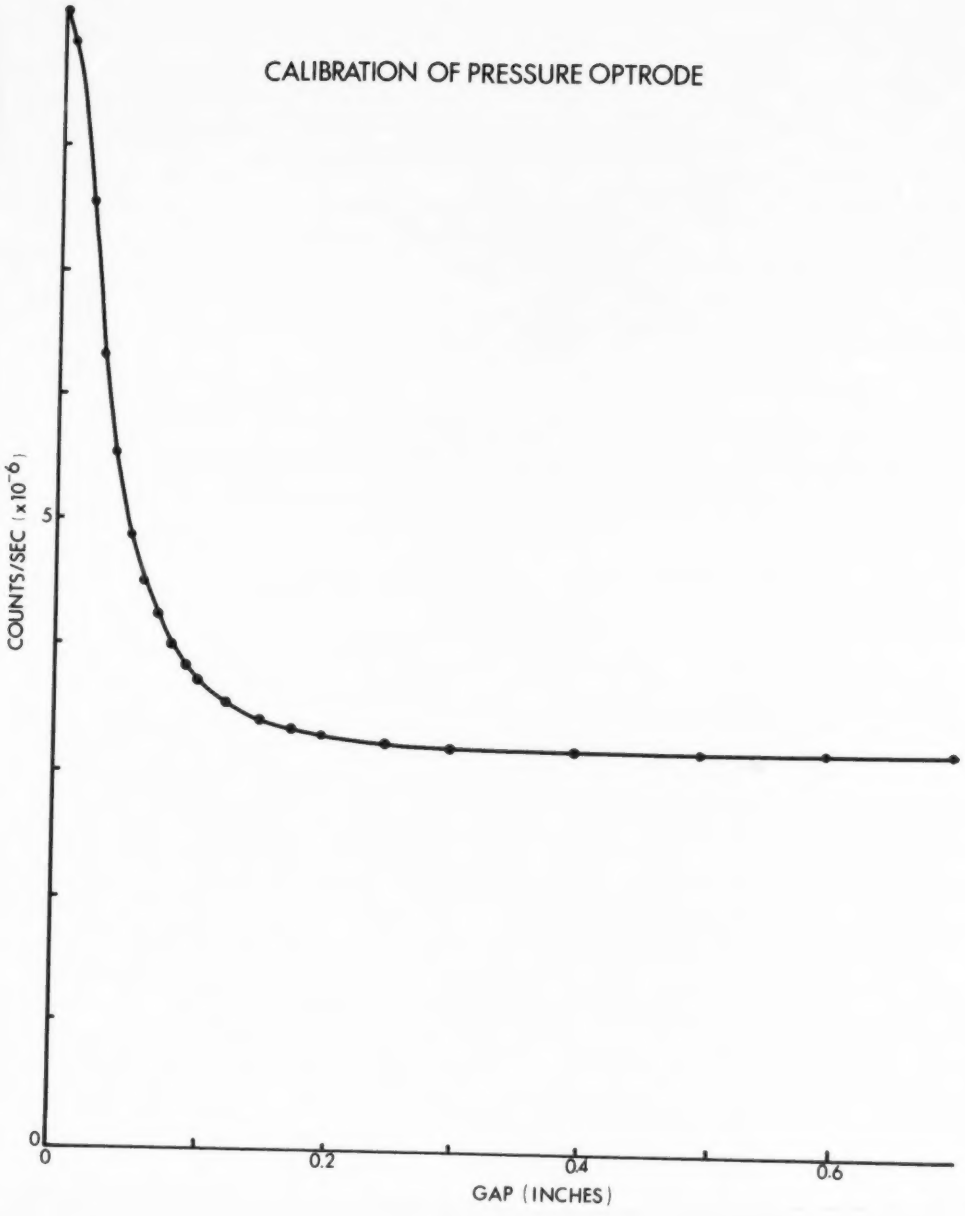


Figure 41. Calibration of pressure optrode.

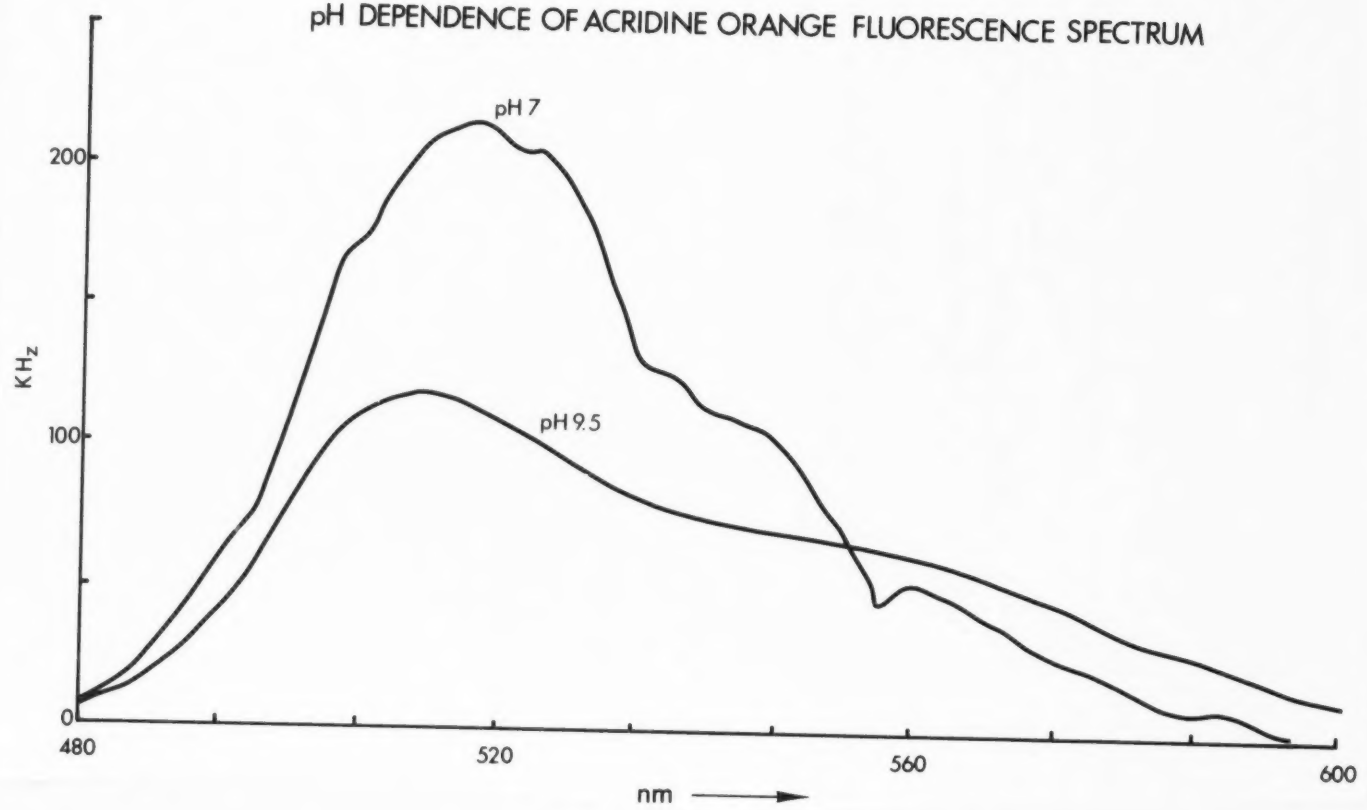


Figure 42. pH dependence of acridine orange fluorescence.

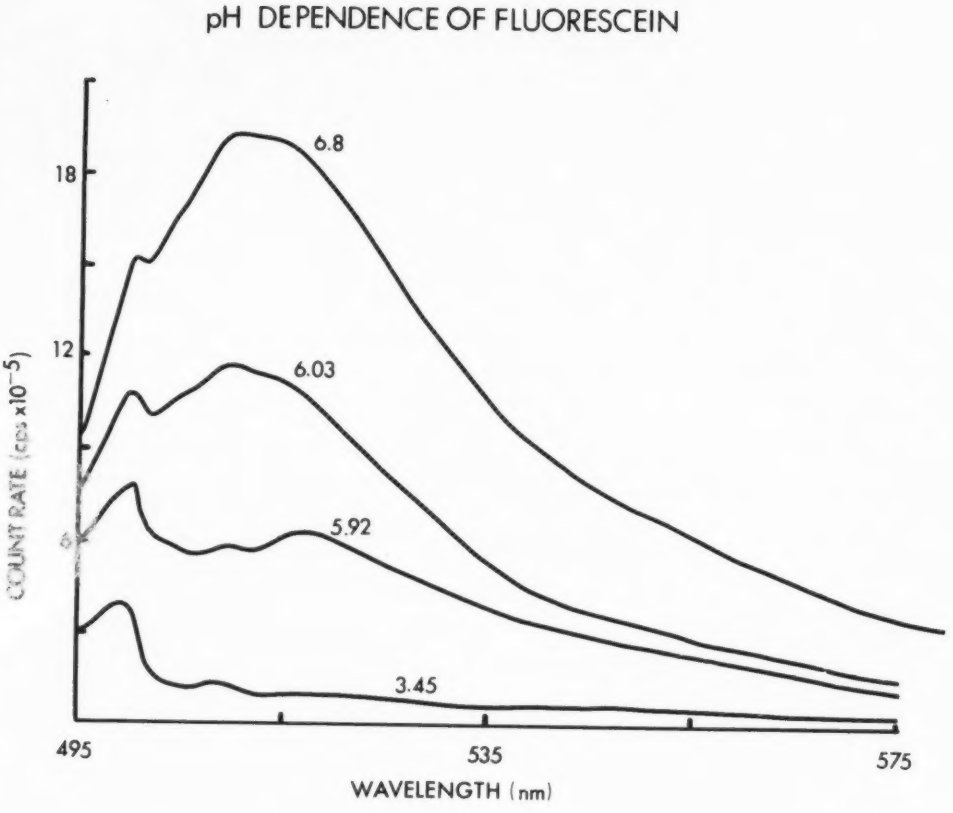


Figure 43. pH dependence of fluorescein fluorescence.

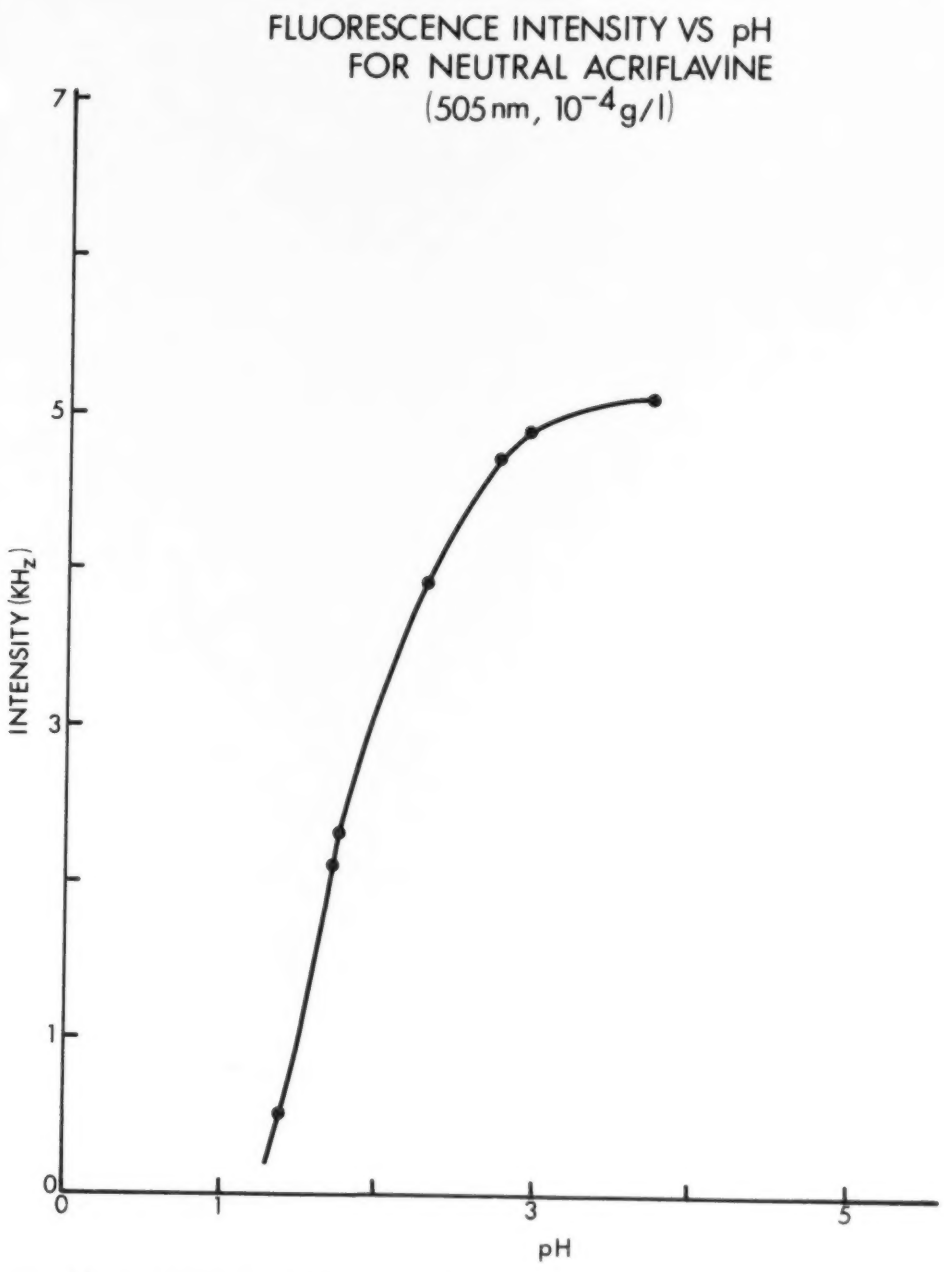


Figure 44. Calibration of neutral acriflavine pH optrode.

SECTION 7

PRELIMINARY ECONOMIC EVALUATION

This is a very preliminary attempt to look at the economic impact of the remote fiber spectroscopy approach. In many instances insufficient information is available and only rough estimates can be made. This analysis is made for 1- and 5-year operation times.

For the purpose of this initial economic analysis, technicaal advantages and considerations have been eliminated. That is to say, no weight is put on the fact that in situ samples have higher integrity than collected ones, and no emphasis has been placed on the advantages of doing the analyses in a laboratory rather than in the field. In addition, it is assumed that there are twenty 100-feet-deep well stations with two species to be analyzed per well and that five areas are to be monitored.

The wells needed for sampling for conventional analysis must be at least 4 inches in diameter. For fiber optics, a well diameter of 1 inch, or less, is feasible. From a practical drilling point-of-view a 1-inch diameter hole in hard rock is reasonable but a 2-inch hole is more practical in sand or clay. For the purpose of this analysis, it is assumed that the wells will be in sand/clay as well as in hard rock. So as not to distort drilling costs, as compared to the charges for analyses, both cases are addressed in Table 3.

TABLE 3. OPERATIONAL SCENARIO FOR GROUNDWATER ANALYSIS

Parameter	Collected Samples	Fiber Optics
Number of areas to be monitored	5	5
Number of wells per area	20	20
Number of species measured per well	2	2
Frequency of analysis (per month)	1	1
Number of years of operation	5	5
Depth of wells (feet)	100	100
Diameter of well-hard rock (inches)	4	1
Diameter of well-sand/clay (inches)	4	2

Table 4 presents the individual cost components of the conventional (collected samples) and fiber optic approach. The drilling costs appear to be about double for the larger hole needed for the sampling method. It is assumed that a pump is required for sampling and this accounts for the higher equipment costs for the conventional system. Provisions are, on the other hand, made for fiber optic sensor replacement and these are listed under well equipment costs. For this economic discussion, it is also assumed that the laboratory providing the conventional analyses will have the necessary equipment available and that all costs for this equipment and its depreciation are included in the single sample price. In the case of the fiber optic system, new equipment will have to be built and mounted in a mobile van. The costs for this are projected to be $60,000 (instruments - $30,000, van - $12,000, and mounting - $18,000). This equipment should be written off in 3 years so that its yearly cost is $18,300. This cost can be divided over several monitoring areas as the equipment is mobile and can be brought to the sampling site.

TABLE 4. INDIVIDUAL COMPONENT COST OF GROUNDWATER ANALYSIS*

Parameter	Cost ($'s) Collected Samples	Cost ($'s) Fiber Optics
Drilling 100-foot well in hard rock	8,000	4,000
Drilling 100-foot well in sand/clay	3,000	1,500
Maintenance 100-foot well/year	200	200
Equipment/well/year/two species	1,000	200
Depreciation/well/year-hard rock	1,840(1)	880(1)
Depreciation/well/year-sand/clay	840(1)	380(1)
Analytical equipment	0(2)	60,000(3)
Maintenance cost analytical equipment/year	0(2)	1,000
Depreciation analytical equipment/year	0(2)	18,000(4)
Cost of individual analyses	125(5)	2(6)

*See Table 3.
(1) Depreciation/year - 0.2 (cost of well + well equipment and maintenance).
(2) Included in Cost of Analyses.
(3) Includes mobile van and installation of equipment in van.
(4) Depreciation/year = 0.3 (cost of analytical equipment plus maintenance.
(5) Analysis costs varies from $150 to $500 per species - $125 is used as a nominal average.
(6) Assumes 1 man at $80/day can do a 20-well area (40 analyses).

In Table 5 all of the inputs are brought together. Here it can be seen that for sampling wells in hard rock, $2,620,000 will be spent for 5 years analysis as compared to only $555,500 for fibers, a difference of over

$2 million. In sand/clay the comparison is $2,120,000 to $305,500 or a difference of nearly $1.8 million. The great advantage of the fiber optic system, as shown by the selected cases, makes it imperative to look at, from the point-of-view of the fibers, a worst-case situation (1 site, 1 year monitoring in sand/clay, depreciate everything in 1 year) and a best-case opportunity (20 sites, 5-year monitoring in hard rock, depreciate everything in 5 years). In the first case, using the same calculations from which Table 5 was generated, the conventional method would cost $148,000 vs. $100,000 for the fiber - still a moderate advantage. In the best situation, however, the sampling approach would be prohibitive at $57,000,000 as compared to $2,500,000 for the fiber optic approach. Thus, except where only a very few wells are to be monitored, the fiber optic approach has obvious economic advantages. Using the previously mentioned worst case conditions, the number of wells would have to be less than 12 before the sampling method has an economic edge.

TABLE 5. COST COMPARISON BETWEEN ANALYSES USING COLLECTED SAMPLES AND IN SITU MEASUREMENTS USING FIBER OPTICS (1 YEAR AND 5 YEARS)*

Parameter	Cost ($'s) Collected Samples	Cost ($'s) Fiber Optics
Yearly cost for 100 wells-hard rock	184,000(2)	88,000(2)
Yearly cost for 100 wells-sand/clay	84,000(2)	38,000(2)
5-Year cost for 100 wells-hard rock(1)	920,000(2)	440,000(2)
5-Year cost for 100 wells-sand/clay (1)	420,000(2)	190,000(2)
1-Year cost for analytical equipment	0(3)	18,300
5-Year cost for analytical equipment	0(3)	91,500(2)
1-Year cost for analyses(4)	340,000(5)	4,800(6)
5-Year cost for analyses(4)	1,700,000(5)	24,000(6)
Total monitoring cost/year-hard rock	524,000(7)	111,100(7)
Total monitoring cost/year-sand/clay	424,000(7)	61,100(7)
Total monitoring cost/5 years-hard rock	2,620,000(7)	555,500(7)
Total monitoring cost/5 years-sand and clay	2,120,000(7)	305,500(7)

*See Table 4.
(1) 5 areas of 20 wells each equal 100 wells.
(2) Based on yearly depreciation cost.
(3) Included in Cost of Analysis.
(4) 5 areas, 20 wells, 2 species per well and 12 analyses/species/year or 2,400 analyses/year.
(5) Based on $125/analysis.
(6) Based on 1 man at $80/day per area (5 days/month or 60 days per year).
(7) Total depreciated well cost and depreciated equipment cost plus analysis cost.

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APPENDIX A

SIGNAL LEVELS IN DISTAL FIBER-OPTICS FLUORIMETRY

At the distal end of a fiber the apex angle of the cone-shaped illuminated volume (Figure A-1) is

$$\alpha = \arcsin \frac{NA}{n_s} \tag{A-1}$$

where

α = apex angle,
NA = numerical aperture of fiber,
n_s = refractive index of sample.

The effective path length in the sample medium, normalized to the illumination intensity and collection efficiency, can be shown to be

$$L_E = \frac{0.727\ d}{\tan \alpha} = 0.727\ d \left(\frac{n_s}{NA} \right)^2 - 1 \Bigg)^{1/2} \tag{A-2}$$

where

L_E = effective path length,
d = diameter of fiber.

The collection efficiency at the fiber face is

$$G = \frac{1 - \cos \alpha}{2} \tag{A-3}$$

where

G = collection efficiency.

ILLUMINATION IN SIMPLE TERMINATION FOR REMOTE FIBER FLUORIMETER

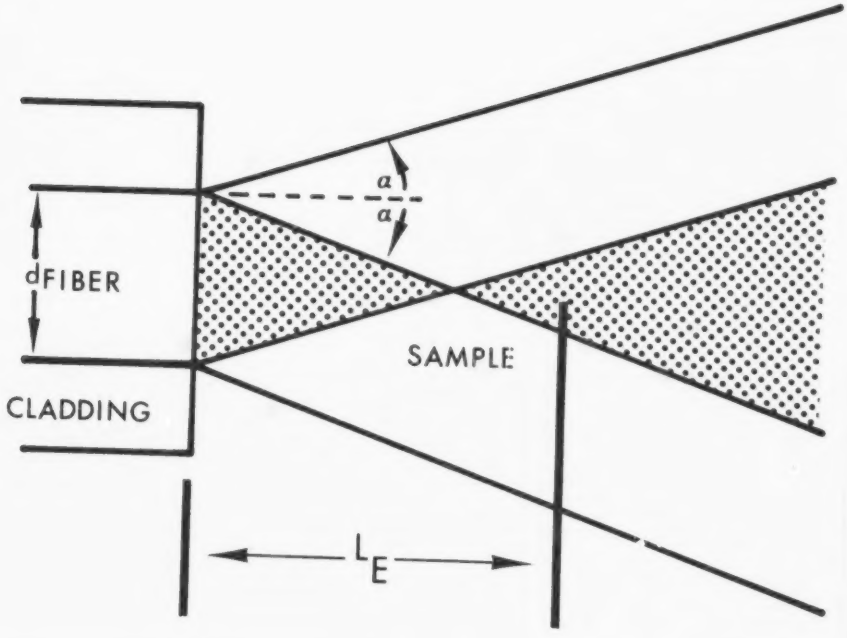

Figure A-1. Illumination in simple termination for remote fiber fluorimeter.

For weekly absorbing samples the fraction of power absorbed in a length, L_E is

$$\frac{\Delta\phi}{\phi} = MCL_E \qquad \text{(A-4)}$$

where

ϕ = total photon flux of the laser beam,
$\Delta\phi$ = fraction of power absorbed,
M = molarity,
C = molar absorption coefficient.

The effective photon yield at the distal end of the fiber (fluorescent photons into the fiber per laser photon out its distal end)

$$Y = G\,Q_F\,\frac{\Delta\phi}{\phi} = G\,Q_F L_E CM. \qquad \text{(A-5)}$$

where

Q_F = sample fluorescence quantum efficiency.

The photon flux at the end of the fiber is related to the laser power P by

$$\Phi = P\,\frac{\lambda}{hc}\,T_{FE}T_I^2\,e^{-a_1 R} \qquad \text{(A-6)}$$

where

P = laser power,
T_{FE} = transmission through excitation filter and beam handling optics,
T_I = transmission through fiber termination,
h = Planck's constant,
λ = laser wavelength,
c = velocity of light,
a_1 = attenuation coefficient for fiber at laser wavelength, and
R = range (fiber length).

The flux of fluorescent photons at the distal end of the fiber is

$$\Phi' = \Phi Y = 0.727\,P\,\frac{\lambda}{hc}\,T_{FE}\,T_I^2\,e^{-a_1 R}\,GQ_F\,CMd\left(\frac{n_s}{NA}-1\right)^{2}\,1/2 \qquad \text{(A-7)}$$

where ' = the flux of fluorescent photons at the distal end of the fiber.

The count rate S from the photodetector is then

$$S = \Phi' (T_I)^2 \, e^{-a_f R} \, T_{FR} \, Q_E \, , \qquad \text{(A-8)}$$

where

S = count rate from the photo detector
a_f = fiber attenuation coefficient at fluorescent wavelength,
T_{FR} = receiver filter transmission, and
Q_E = detector quantum efficiency.

If typical parameters are substituted into the previously developed equations it can be shown that the fiber system (without optrodes) has sub-parts-per-million capability. This can be demonstrated by using the following inputs:

P	= 1 W,	d	= 0.4 mm,
λ	= 674.1 nm,	G	= 0.023
T_{FE}	= 0.64,	Q_F	= 0.1,
T_I	= 0.9,	C	= 60,
R	= 1000 m,	M	= 10^{-6} M,
α_1	= 2.3/km,	n_s	= 1.334,
α_f	= 1.15/km,	NA	= 0.4, and
Q_E	= 0.1,	T_{FR}	= 0.25,

which yield $S = 1.5 \times 10^8$ photoelectrons/second, an easily measureable signal.

APPENDIX B

MISALIGNMENT TOLERANCE IN REMOTE FIBER FLUORIMETRY

The transmission across an optical fiber junction having a negligible gap is

$$T = \frac{A}{\pi r^2} \tag{B-1}$$

where

A = overlap area between fibers,
r = fiber radius.

A can be calculated as the sum of two identical segments each of which is

$$\frac{A}{2} = \theta r^2 - \frac{s}{2} r \sin\theta, \tag{B-2}$$

where

s = misalignment,
θ = half central angle of segment

then

$$\theta = \arccos \frac{s}{2r}. \tag{B-3}$$

and by substitution

$$T = \frac{1}{\pi} 2 \arccos \frac{s}{2r} - 2 \frac{s}{2r} \sqrt{1 - \left(\frac{s}{2r}\right)^2}. \tag{B-4}$$

If the relative misalignment is defined as

$$x = \frac{s}{2r}, \tag{B-5}$$

where

$$x = \text{relative misalignment},$$

then equation (B-4) becomes

$$T = \frac{2}{\pi} \arccos x - x\sqrt{1 - x^2} \quad . \tag{B-6}$$

The efficiency loss can be written as

$$E = T^2 \tag{B-7}$$

and the misalignment loss can be tabulated as shown in Table B-1.

The same approach can be applied in angular space and equation B-6 and Table B-1 are valid with the substitution,

$$r = \arcsin \frac{NA}{\eta} , \tag{B-8}$$

TABLE B-1. MISALIGNMENT LOSS IN REMOTE FIBER FLUORIMETRY

Relative Misalignment (x)	Junction Transmission (T)	Efficiency Loss (E)
0	100%	100%
0.01	98.73	97.48
0.02	97.45	94.97
0.05	93.64	87.68
0.10	87.29	76.20
0.20	74.41	55.82
0.30	62.38	38.91
0.40	50.46	25.46
0.50	39.10	15.29
0.60	28.48	8.111
0.70	18.81	3.538
0.80	10.41	1.084
0.90	3.738	0.1397
1.00	0.0	0.0

where

NA = fiber numerical aperture and
η = index of gap medium

The angular misalignment is then

$$X = \frac{X}{2r} = \frac{X}{2 \arcsin \frac{NA}{\eta}} . \qquad \text{(B-9)}$$

where

X = angular misalignment.

APPENDIX C

CONVECTION-DRIVEN CAPILLARY OPTRODE SAMPLING

The thermal expansion head for a capillary in the vertical position is

$$h_T = (L - L_G/2)\,\Delta T \rho \beta \qquad \text{(C-1)}$$

where

h_T = thermal expansion head
L = length of capillary
L_G = length of heating region
ΔT = temperature increase
ρ = sample density
β = sample volume thermal-expansion coefficient.

From Bernoulli

$$h_T = h_V + h_F \qquad \text{(C-2)}$$

where

h_V = velocity head and
h_F = friction head.

Then

$$h_V = \frac{v^2}{g} \qquad \text{(C-3)}$$

where

g = acceleration of gravity
v = sample velocity

and

$$h_V = \frac{32\, v\mu L}{\rho g d^2} \qquad \text{(C-4)}$$

where

μ = sample viscosity

d = capillary diameter.

By substituting for h_T in equation (C-1) it can be shown that

$$L - \frac{L_G}{2} \Delta T \rho \beta = h_T = \frac{v^2}{gp} + \frac{32\, v \mu L}{\rho g d^2} . \qquad \text{(C-5)}$$

A quadratic solution leads to

$$v = \frac{16 \mu L}{d^2} \left[1 + \frac{(L - L_G/2)\ \Delta T \rho^2\ g \beta d^4}{256\ \mu^2\ L^2} \right] - 1 \qquad \text{(C-6)}$$

For cases where v is small, a good approximation is

$$v = \frac{(L - L_G/2\ \Delta T \rho^2 g \beta d^2}{32\ \mu L} . \qquad \text{(C-7)}$$

Using equation (C-7) and realistic parameters such as

L = 10.0 cm,
L_G = 1.0 cm,
ΔT = 20°C,
ρ = 1.0 g/cm^3,
g = 981 g x cm/sec^2,
β = 2.1 x 10^{-4} °C,
d = 1.0 mm, and
μ = 1.0 cp,

v calculates to be 0.12 cm/s. This means the capillary would pump out in 1 1/2 minutes, a reasonable time.